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ANALYTICAL EDITION

Industrial AND ENGINEERING Chemistry

VOLUME 6 NUMBER 1 JANUARY 15, 1934

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HARRISON E. HOWE, EDITOR

Composition of Fatty Acid Mixtures

II. A Further Development of the Twitchell Mixed-Melting-Point Method for Determination of Individual Saturated Fatty Acids

ROBERT N. WENZEL, Mellon Institute of Industrial Research, Pittsburgh, Pa.

THE analytical methods usually applied to the testing of commercial fats and fatty acid mixtures leave the question of their composition, in terms of constituent fatty acids, largely undetermined. Where control of composition is an important factor in the success of commercial processes, as in the growth of crystals in molten fatty acid mixtures, reliance must therefore be placed largely on empirical formulas for the blending of fats of different grades and different sources. Blending formulas are not always dependable, however, because the raw materials themselves are usually subject to considerable variation. Again, in industrial research, analyses of fatty acid mixtures are frequently of service only in so far as they can be interpreted in terms of composition. Such interpretation, based solely on resultant properties of the mixture—total unsaturation, acid value, titer, etc.—is at best uncertain and often quite misleading. There is need therefore for methods that determine, specifically, the percentages of individual fatty acids present.

THE MIXED-MELTING-POINT METHOD

In view of this situation, the mixed-melting-point method devised by Twitchell (*11*) has certainly not received the attention that its possibilities would seem to merit.

The method is based on the fact that if a sample consisting of a mixture of fatty acids is added to a single pure fatty acid only those acids in the mixture that are not identical with the pure acid solvent will be effective in lowering its melting point. Twitchell reasoned that, because of their uniformly high molecular weights, all the fatty acids should have approximately equal effect in depressing the melting point of any solvent. Thus, if the solvent acid is stearic, the depression of the melting point gives a measure of all acids other than stearic acid in the mixture. From this the percentage of stearic acid in the sample is readily calculated.

As used by Twitchell, the method was subject to serious limitations, mainly because the melting-point determination itself was not sufficiently precise to permit the establishment of accurate, specific depression constants for the different individual acids. In addition, Twitchell measured all depressions at 20 per cent of total solute acids. This not only necessitated a preliminary trial, in each analysis, before weighing out the final mixture, but it placed the measurements beyond the straight-line portion of the melting-point curve and therefore outside the range in which melting-point data can properly be applied.

The method was later used by McGregor and Beal (*8*), in their study of the fatty acids of menhaden oil, in essentially the form in which it was left by Twitchell.

A distinct improvement in the results obtainable by the mixed-melting-point method is made possible by an improved melting-point technic here described. Specific depression constants have been determined by measurements on binary mixtures of pure acids, including stearic, palmitic, myristic, and oleic. It has been found that depressions in palmitic acid and in stearic acid are apparently controlled, as might be expected, by definite molar depression constants characteristic of the solvent acid and independent of the solute. Reliable specific depression constants for the individual solute acids can thus be based on the molar constant for the solvent and the molecular weight of the solute. For solutions in myristic acid, the behavior of dissolved stearic acid is apparently anomalous, giving a molar depression constant higher than that obtained when the solute acid is palmitic or oleic. This departure from the theoretical has not been explained. For stearic acid in myristic, therefore, the specific depression constant directly determined must be accepted. The proper depression constant to use in any particular analysis is readily calculated from the specific constants here established.

The method gives results only reliable to within a few per cent, but, in spite of its limited accuracy, is an extremely valuable tool. As here worked out, it has proved very useful in the investigation of problems encountered in the manufacture of commercial fatty acids, particularly in defining the limits of toleration of the crystallizing process to variations in the composition of the stock.

THE MELTING-POINT DETERMINATION

Even in the case of pure compounds, melting points depend largely on apparatus and technic. Thus widely differing values for the melting point of any of the pure fatty acids will be found in the literature. With fatty acid mixtures there is the further difficulty that here we are dealing with a case of solid solutions. The composition–melting-point

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diagram for mixtures of two fatty acids is not a single line, but two lines, the so-called liquidus and solidus curves. Even with the maintenance of ideal equilibrium conditions, melting will start at one temperature and continue over a considerable range of values; and at any temperature within this range the mixture exists as a perfectly stable, two-phase system.

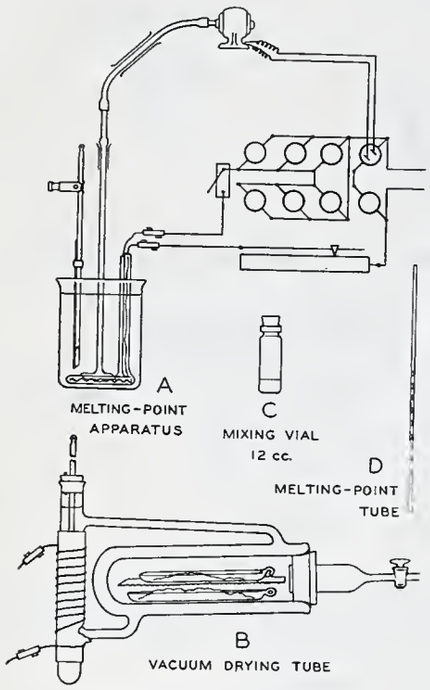

Figure 1. Apparatus

Theoretically, both the initial and final temperatures of this melting range are characteristic properties of the mixture. Practically, it is only the final point that can be determined with any accuracy. The point usually recorded in melting-point determinations—i. e., the temperature at which clear liquid first appears in the sample—comes at neither the beginning nor the end of the melting range, but depends upon the rate at which the solid settles through the liquid first formed. In the present work, final temperatures were therefore used throughout.

McGregor and Beal, as well as Twitchell, allowed the material in the melting-point tube to stand for at least 12 hours to remove strain before the melting point was taken. The necessity for this precaution in the case of fats has been pointed out by Lewkowitsch (*7*), Bloor (*2*), and others. Burks (*3*) found, however, that the double melting points exhibited by recently melted glycerides are not encountered in the case of the free fatty acids.

Burks' observations are confirmed by the following series of melting-point readings taken on the same sample after exposing the tube to the various treatments indicated. The two readings recorded in each case were taken at the first appearance of clear liquid and at the disappearance of the last of the solid.

	° C.
Initial melting point	60.76 to 61.08
After solidifying and standing 43 hours at room temperature	60.88 to 60.98
After solidifying and again standing 52 hours at room temperature	60.90 to 61.10
After keeping melted in an oven at 65° to 70° C. for 17 hours and standing at room temperature 45 minutes	60.94 to 61.14
After cooling to, and holding at 55.5° to 57.5° C. for 4 hours	60.97 to 61.14
After plunging into ice water, holding there 5 minutes, and repeating the melting-point determination at once	60.73 to 61.15

It will be seen that the melting point is not appreciably affected by repeated melting, long standing at room temperature, long continued heating just above the melting point, slow solidification just below the melting point, or rapid solidification in an ice bath. We may therefore conclude that there is no decomposition at the melting point to necessitate a rapid melting-point determination and that there is nothing to be gained by aging the sample in the melting-point tube.

Burks recommended an extremely slow rate of heating designed to simulate immersion of the sample tube for two minutes in each of a succession of constant-temperature baths differing by only 0.1° C. This procedure was adopted in the present work because it makes possible a high degree of precision in the melting-point determination. The apparatus used is, in all its essential features, identical with that employed by Burks.

In order to obtain the sharp temperature control required, it is essential to use a closed melting-point tube immersed directly in the temperature bath. Twitchell's ingenious method of loading an open tube from the melted mixture, to insure a true sample, and then giving it a sharp jar, so that the sample solidifies as a string of short segments, has been retained, but the tube is then sealed in the Bunsen flame. With proper precautions this can be done without injuring the sample.

Apparatus

Figure 1A is a diagram of the apparatus used for the melting-point determinations. A 600-cc. Pyrex beaker containing water or a light, colorless mineral oil serves as the heating bath. The immersion heater consists of a spiral coil of resistance wire sheathed in a loop of Pyrex glass tubing. The lamp bank and rheostat connections are indicated. The beaker is not insulated, as accurate temperature control depends upon a nice balancing of heat input against radiation, but it must be protected from fitful air drafts. Two melting-point tubes are fastened to the thermometer by means of a rubber band. In addition, a fork made of glass tubing, with two prongs extending into the bath parallel to the thermometer, makes it possible to introduce six tubes at a time. The slow rate of heating allows ample time for observing and recording the behavior of each sample.

The melting-point thermometers used are of ranges 20° to 60° C. and 40° to 80° C., graduated in 0.1° units and calibrated by comparison with thermometers certified by the United States Bureau of Standards. A magnifying attachment permits readings to 0.01° C. Emergent stem temperatures are also recorded.

The exact size of the melting-point tube is not critical. Tubes of inside diameter such as to accept a No. 22 B & S gage wire but not a No. 20 wire were selected. A small hand lens is used to observe the behavior of samples during melting.

It is of course essential that the fatty acids be dry. A convenient device for thorough and rapid drying of small samples, also suggested by Burks, is the vacuum drying tube shown in Figure 1B. The drying chamber is divided into upper and lower compartments by a screen of heavy wire gauze. Samples are placed in the upper compartment, phosphorus pentoxide in the lower. Water circulated through the jacket is heated in the upright tube, either electrically or by means of a small gas flame, and the temperature maintained at a point only a few degrees below the melting point of the sample. The tube is evacuated by means of an oil pump. Thorough drying is accomplished within 15 or 20 minutes in this apparatus.

Procedure

Each analysis is run in duplicate, two mixtures with definitely different proportions of sample and pure acid being prepared. The mixture, weighing usually about 2 grams, is weighed out in a small square-shouldered vial of 12 cc. capacity (Figure 1C) and melted down in an oven at 100° C. Mixing is effected by tilting the vial until the liquid reaches the shoulder, rotating it in this position and shaking.

Two open melting-point tubes are then dipped into the mixture. Following Twitchell's technic, the sample in each tube is broken into a string of small uniform segments and, by proper manipulation above the flame, the last segment is spaced about 7 mm. from the end of the tube. By

TABLE I. MELTING-POINT DEPRESSIONS IN PALMITIC AND STEARIC ACIDS

Mixture	Percentage Composition of Mixture: Palmitic acid	Stearic acid	Oleic acid	Mole Per Cent Total Solute	Melting Point ° C.	Melting-Point Depression, L	$10L \div$ Wt. Per Cent Solute, K_w	$10L \div$ Mole Per Cent Solute, K_m
1	100	...	...	...	62.30	..	..	..
2	95.00	5.00	...	4.52	61.50	0.80	1.60	1.77
3	90.00	10.00	...	9.10	60.62	1.68	1.68	1.84
4	85.00	15.00	...	13.72	59.78	2.52	1.68	1.84
5	80.00	20.00	...	18.38	58.62	3.68	1.84	2.00
6	94.51	...	5.49	4.85	61.44	0.86	1.56	1.77
7	89.99	...	10.01	9.17	60.63	1.67	1.67	1.82
8	84.95	...	15.05	13.84	59.79	2.51	1.67	1.81
9	79.74	...	20.26	18.76	58.79	3.51	1.73	1.87
10	89.67	4.98	5.35	9.44	60.63	1.67	1.62	1.77
11	84.81	4.99	10.20	13.95	59.74	2.56	1.68	1.83
12	84.99	10.00	5.01	13.77	59.79	2.51	1.67	1.82
13	...	100	...	...	69.10	..	..	..
14	5.00	95.00	...	5.52	68.22	0.88	1.76	1.59
15	10.00	90.00	...	10.98	67.39	1.71	1.71	1.56
16	15.00	85.00	...	16.39	66.44	2.66	1.77	1.62
17	20.00	80.00	...	21.74	65.47	3.63	1.82	1.67
18	...	94.91	5.09	5.13	68.26	0.84	1.65	1.64
19	...	89.58	10.42	10.52	67.41	1.69	1.62	1.61
20	...	84.96	15.04	15.18	66.62	2.48	1.65	1.64
21	...	80.01	19.99	20.16	65.72	3.38	1.69	1.68
22	4.99	89.78	5.23	10.74	67.40	1.70	1.66	1.58
23	9.99	84.74	5.27	16.20	66.49	2.61	1.71	1.61
24	4.99	84.83	10.18	15.70	66.58	2.52	1.66	1.61
25	30.00	70.00	...	...	63.20	..	..	..
26	40.00	60.00	...	...	60.33	..	..	..
27	50.00	50.00	...	...	56.71	..	..	..
28	60.00	40.00	...	...	56.20	..	..	..
29	70.00	30.00	...	...	55.50	..	..	..

careful warming, the walls of the end section are now drained completely into the last segment. The tube is then sealed. Sometimes sealing the tube affects the melting point of the last segment, but it can have no effect, of course, on the others. All the segments in both tubes, melting simultaneously, give assurance that a homogeneous mixture has been obtained and that there is no irregularity in the melting point due to accidental factors. The loaded tube is shown in Figure 1D.

In melting the sample, it is heated rapidly to within 1° of the anticipated melting point. If this is not known approximately it is determined by a rapid preliminary melting. From there on the procedure is to hold the temperature constant, within a few hundredths of a degree, for 2 minutes and then allow it to rise 0.1° during the next minute, when it is again held constant for 2 minutes, and so on. The temperature at which the last speck of solid material in each separate portion of the sample disappears is taken as the melting point. Duplicate determinations should agree within 0.05° C.

PREPARATION OF PURE FATTY ACIDS

In order to establish specific depression constants, it was necessary to have samples of the pure fatty acids. In addition, the pure saturated acids are required as reagents in the mixed-melting-point method. The acids used were prepared as follows:

STEARIC ACID. The methyl esters obtained from commercial double-distilled oleic acid were distilled at low pressure through a fractionating column. The first half of the distillate, containing large amounts of methyl palmitate, was rejected. The second portion, boiling at practically constant temperature (174° to 178° C. at 3 mm.) and containing only C_{18} acids, was hydrogenated in 25-gram quantities in alcoholic solution, using platinic oxide as catalyst (*1*). The combined alcoholic solutions were then refluxed 4 hours with 2 *M* equivalents of potassium hydroxide to saponify the esters and the soaps split with hydrochloric acid. The recovered acids, washed free of chlorides, were recrystallized once from petroleum ether and repeatedly from acetone until no further increase in melting point resulted. The product thus obtained consists of beautifully white, crystalline flakes. Samples of melting point 69.0° C. or higher are accepted for use in the mixed-melting-point method.

PALMITIC ACID. Fatty acids recovered from bayberry wax were converted to their methyl esters and distilled at low pressure through an efficient fractionating column. The first 40 per cent of the distillate was rejected. The remainder, coming over at constant temperature, was treated for recovery of the acids which were then recrystallized from acetone. Preparations having melting points of 62.0° C. or higher are accepted.

MYRISTIC ACID. Nutmeg butter, obtained from ground nutmegs by extraction with ether after a preliminary alcohol extraction had removed most of the color and the volatile oil, was saponified and the soap solution acidified to liberate myristic acid. Recrystallized three times from acetone, the acid melted at 53.32° C. This product was distilled under reduced pressure and the first and last fractions were rejected. The remainder, again recrystallized from acetone, was recovered in two fractions melting at 54.17° and 53.88° C., respectively.

OLEIC ACID. Preparation of oleic acid of a high degree of purity is a matter of considerable difficulty. It was required here for the determination of melting-point depression constants, but is not required as a reagent in the mixed-melting-point method.

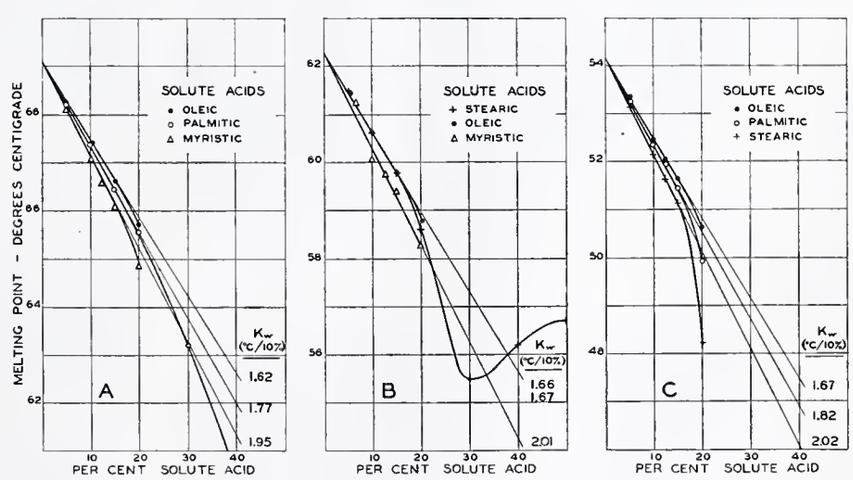

FIGURE 2. MELTING-POINT DEPRESSIONS

A, in stearic acid *B*, in palmitic acid *C*, in myristic acid

Olive oil fatty acids were used as the source of oleic acid. Most of the saturated acids were removed by Twitchell's lead soap–alcohol method (*10, 12*). Removal of most of the linoleic acid was effected by refluxing the unsaturated acids in alcohol, with enough finely ground solid barium hydroxide to convert 80 per cent of the acids to their barium soaps, thus leaving the linoleic acid, together with some oleic, in solution. This is a modification of the procedures of Farnsteiner (*5*) and of Lapworth and Pearson (*6*). For the final purification from small amounts of palmitic acid and linoleic acid, fractional crystallization of the lithium soaps according to Scheffers (*9*) was adopted. This method was found more effective in removing linoleic acid, however, than in concentrating palmitic acid in the first fractions.

Table II. Melting-Point Depressions in Mixtures Involving Myristic Acid

Mixture	Weight of Acids in Mixture: Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Weight Per Cent Solute	Mole Per Cent Solute	Melting Point	Melting-Point Depression, L	$10L \div$ Weight Per Cent Solute, K_w	$10L \div$ Mole Per Cent Solute, K_m
	Grams	*Grams*	*Grams*	*Grams*			° *C.*			
30	....	1.0000	....	....	0.00	...	62.45	..	..	..
31	0.1152	1.9286	....	....	5.64	6.28	61.39	1.06	1.88	1.69
32	0.2026	1.8089	....	....	10.07	11.17	60.53	1.92	1.91	1.72
33	0.2604	1.7523	....	....	12.94	14.30	59.88	2.57	1.99	1.80
34	0.3016	1.7062	....	....	15.02	16.56	59.53	2.92	1.94	1.76
35	0.4040	1.6008	....	....	20.05	22.08	58.42	4.03	2.01	1.82
36	....	....	1.0000	....	0.00	...	69.21	..	..	..
37	0.1003	....	1.9045	....	5.00	6.16	68.20	1.01	2.02	1.64
38	0.2034	....	1.8003	....	10.15	12.34	67.19	2.02	1.99	1.64
39	0.2514	....	1.7500	....	12.53	15.17	66.68	2.53	2.02	1.67
40	0.3011	....	1.7012	....	15.04	18.05	66.18	3.03	2.01	1.68
41	0.4005	....	1.6005	....	20.01	23.75	64.97	4.24	2.12	1.79
42	1.0000	....	....	....	0.00	...	54.17	..	..	..
43	1.9015	0.1007	....	....	5.03	4.50	53.26	0.91	1.81	2.02
44	1.8029	0.2000	....	....	9.99	8.99	52.35	1.82	1.82	2.02
45	1.7519	0.2506	....	....	12.51	11.30	51.95	2.22	1.77	1.96
46	1.7029	0.3026	....	....	15.09	13.66	51.45	2.72	1.80	1.99
47	1.6019	0.4019	....	....	20.06	18.26	49.93	4.24	2.11	2.32
48	1.9002	....	0.1018	....	5.08	4.12	53.16	1.01	1.99	2.45
49	1.8057	....	0.2014	....	10.03	8.22	52.15	2.02	2.01	2.46
50	1.7498	....	0.2500	....	12.50	10.29	51.65	2.52	2.02	2.45
51	1.6998	....	0.2995	....	14.98	12.39	51.14	3.03	2.02	2.44
52	1.6008	....	0.4024	....	20.09	16.79	48.24	5.93	2.95	3.53
53	1.9044	....	....	0.1024	5.10	4.17	53.36	0.81	1.75	1.94
54	1.8009	....	....	0.2023	10.10	8.33	52.46	1.71	1.69	2.08
55	1.7581	....	....	0.2510	12.49	10.35	52.05	2.12	1.70	2.04
56	1.7026	....	....	0.3019	15.06	12.54	51.65	2.52	1.67	2.01
57	1.6038	....	....	0.4021	20.05	16.86	50.64	3.53	1.76	2.10

Fractional distillation of the free acid, under reduced pressure and in an atmosphere of nitrogen, with rejection of a considerable first fraction, was finally resorted to and should preferably precede the lithium soap recrystallizations.

In the Scheffers lithium soap procedure, the successive recrystallizations are made after combining fractions of like iodine value. For this purpose Scheffers withdraws samples from which he liberates and recovers the free acids for analysis. The lithium soaps, however, can be dried at 110° C. without change and they are freely soluble in glacial acetic acid. Iodine values can therefore be taken directly on the lithium soaps, and much time and labor are thus saved.

The only satisfactory criterion of purity in the final oleic acid is to separate it by distillation through an efficient column into a number of fractions, all of which agree in iodine value with the theoretical. The product eventually obtained was a sparkling liquid, perfectly colorless and odorless, with an iodine value of 89.6.

Determination of Specific Depression Constants

Data from which melting-point depression constants were computed for solutions in palmitic and stearic acids are given in Table I. Similar data are given in Table II for mixtures involving myristic acid. The calculated specific depression constants, K_w, here defined as the lowering in degrees Centigrade per 10 per cent by weight of solute, and the molar constants, K_m, expressed in degrees Centigrade per 10 per cent mole fraction of solute, are also tabulated.

Inspection of Table I shows at once that for either solvent a single molar depression constant applies, irrespective of the solute. Rejecting the values for 20 per cent of solute, which are high in every case, nine values of K_m for palmitic acid average 1.81 with an average deviation of 0.02, and nine values for stearic acid average 1.61 with an average deviation also 0.02. Discounting the results for only 5 per cent of solute, since these involve a higher experimental error, the accepted values are 1.82 and 1.61, respectively.

Using these molar constants and the molecular weights of the solute acids, we arrive at the numerical values shown in Figures 2A and 2B for the respective specific depression constants. The data points and curves show how well and how far the measured depressions follow these constant slopes.

Since the molar depression constants 1.82 and 1.61 for palmitic and stearic acids, respectively, are almost exactly in the inverse ratio of their molecular weights, it might seem reasonable to expect that the value of K_m for myristic acid would be found at about 2.02:

K_m		Mol. Wt.		
1.82	×	256	=	466
1.61	×	284	=	457
		Av.		461.5

461.5/228 = 2.02

This value is approximated very closely by solutions of palmitic acid and oleic acid in myristic, but solutions of stearic acid in myristic give a higher value—namely, 2.45. The specific depression constants shown in Figure 2C for palmitic acid and oleic acid were derived from the molar constant 2.02 for myristic acid and the molecular weights of the solute acids. For stearic acid in myristic, the value of K_w directly measured—namely, 2.02—is shown.

Sample Analysis

The manner of applying these depression constants in the determination of individual saturated acids is illustrated in the following example. The analytical data are given in Table III.

Table III. Data, Sample Analysis

Solvent acid	Palmitic		Stearic		Myristic	
Mixture No.	1	2	3	4	5	6
Weight of sample, gram	0.1404	0.1496	0.1412	0.1522	0.1457	0.1542
Weight of solvent acid, gram	0.8600	0.8590	0.8678	0.8603	0.8890	0.8837
Weight of mixture, gram	1.0004	1.0086	1.0090	1.0125	1.0347	1.0379
Per cent sample (a)	14.03	14.83	13.99	15.03	14.08	14.86
Melting point of mixture, ° C.	60.12	60.02	67.18	66.98	51.44	51.24
Melting point of solvent acid, ° C.	61.93	61.93	69.21	69.21	53.88	53.88
Depression, ° C. (L)	1.81	1.91	2.03	2.23	2.44	2.64

This sample was obtained in the commercial processing of tallow fatty acids. It is known therefore to be essentially a mixture of palmitic, stearic, and oleic acids, with, possibly, smaller amounts of linoleic and myristic whose net effect on the melting-point depression rates may be neglected. For solutions in palmitic acid, the specific depression constants for stearic and oleic are practically identical, the values found being 1.66 and 1.67. Using the average value 1.665, we arrive at the following results for palmitic acid:

	Mixture 1	Mixture 2	Average
Per cent not palmitic in mixture ($10L/1.665$)	10.87	11.47	..
Per cent sample in mixture (a)	14.03	14.83	..
Per cent sample palmitic in mixture (b)	3.16	3.36	..
Per cent palmitic acid in sample (b/a)	22.5	23.2	22.8

In calculating the percentage of stearic acid in the sample, the value of K_w to be used will lie between 1.62 for oleic and 1.77 for palmitic at a figure depending upon the proportions of these

two acids in the sample. Since the palmitic acid content is now known and the total acids other than stearic can be approximately determined by the use of a trial value, say 1.7, for the depression rate, the proper value of K_w to use can be determined as follows:

	Mixture 3	Mixture 4	Average
Per cent acids other than stearic in sample (10 L/1.7 a)	85.4	87.4	86.4
Per cent palmitic acid in sample	..	..	22.8

$$K_w = 1.62 + (22.8/86.4)\ (1.77 - 1.62) = 1.62 + 0.04 = 1.66$$

The results of the analysis for stearic acid are then as follows:

	Mixture 3	Mixture 4	Average
Per cent not stearic in mixture (10 L/1.66)	12.23	13.42	..
Per cent sample in mixture (a)	13.99	15.03	..
Per cent sample stearic in mixture (b)	1.76	1.61	..
Per cent stearic acid in sample (b/a)	12.6	10.7	11.6

For myristic acid the procedure is the same except that here three acids must be considered: palmitic, stearic, and oleic, for which the specific depression constants in myristic acid are respectively 1.82, 2.02, and 1.67. The approximate proportions of these three acids in the sample will determine the value of K_w to be used. Making use here of the figures 22.8 per cent palmitic, 11.6 per cent stearic and the free fatty acid value which was found by titration to be 99.3 per cent as oleic acid—i. e., 99.3 per cent expressed on the basis of an average molecular weight of 282—the proper value of K_w is found as follows:

Per cent palmitic, as oleic (22.8 × 282/256)				25.1
Per cent stearic, as oleic (11.6 × 282/284)				11.5
Sum				36.6
Per cent total free fatty acids, as oleic				99.3
Per cent remaining acids, largely oleic, as oleic				62.7
	%	K_w		
Palmitic acid	22.8 ×	1.82 =	41.5	
Stearic acid	11.6 ×	2.02 =	23.4	
Oleic acid	62.7 ×	1.67 =	104.6	
	97.1		169.5/97.1 = 1.75	

The results for myristic acid are then as follows:

	Mixture 5	Mixture 6	Average
Per cent not myristic in mixture (10 L/1.75)	13.93	15.10	...
Per cent sample in mixture (a)	14.08	14.86	...
Per cent sample myristic in mixture (b)	0.15	−0.24	...
Per cent myristic acid in sample (b/a)	1.1	−1.6	−0.2

While very close checks are often obtained, the mixed-melting-point results are not accurate to more than a few per cent. Especially in determining small amounts of acid, duplicate analyses may fail to agree within 5 per cent or even more. The values here found for myristic acid are totally without significance except to show that myristic acid is probably absent from this sample.

It might at first appear that these low results for myristic acid must necessarily follow from the fact that there has been no allowance for myristic acid in determining the value of K_w employed. On the contrary, however, one might allow for a considerable percentage of myristic acid, say 15 per cent, without greatly affecting either the value of K_w that would be chosen or the final analytical results. Thus, if the acids determined above, by difference, as 62.7 per cent oleic are assumed to consist of only 47.7 per cent oleic and 15 per cent myristic (as oleic), the total percentage of acids other than myristic becomes 82.1 instead of 97.1, their total per cent × K_w product becomes 144.6, the resulting value of K_w becomes 1.76, and the calculated percentages of myristic acid in the sample are 1.6 and −0.95, averaging 0.3 per cent. Of course, should the sample prove to contain a considerable percentage of myristic acid, this must also be taken into account when estimating K_w values to be used in determining the other saturated acids.

Importance of Proper Selection of K_w Values

The results obtained by this method are dependent, in part, upon the proper selection of the K_w value to be used in each case and the determination of this value, which is based on the specific depression constants for the pure acids, as indicated above, requires also some preliminary knowledge of the chief constituent fatty acids present and their approximate proportions. The analyst will usually have sufficient information of this sort about his samples to lead him to the proper constants. If not, however, the approximate composition is readily obtained by a preliminary examination of the melting-point data, using trial constants.

It is not likely, therefore, that any considerable error in the assignment of K_w values will be made. Nevertheless, it is of interest to note the magnitude of the errors that can be introduced into the final results by the use of wrong constants.

Let us assume that the sample being analyzed consists entirely of palmitic and stearic acids and that, after mixing with pure stearic acid, the composition of the mixture is 85 per cent stearic and 15 per cent palmitic. The melting-point depression is 2.66 degrees. The proper K_w value to use is 1.77. Suppose, however, that the value 1.70 is used instead. The calculation would then indicate 10 × 2.66/1.70 or 15.65 per cent of acids other than stearic and therefore 84.35 per cent of stearic acid in the mixture. Expressed as a percentage of the original sample, the error would be considerably magnified, depending upon the ratio of sample to pure acid used in making up the melting-point mixture or, in other words, upon the percentage of stearic acid in the sample. The proportions it might thus reach are shown in Table IV, where five different cases are assumed.

Table IV. Effect of Error of 0.07 in Value of K_w

Stearic Acid in Sample	Composition of Mixture: Pure stearic a	Composition of Mixture: Sample b	Stearic Acid in Mixture	Found in Mixture c	Calculated in Sample $(c-a)/b$	Error in Per Cent of Sample
%	%	%	%	%	%	
5	84.21	15.79	85	84.35	0.9	4.1
10	83.33	16.67	85	84.35	6.1	3.9
20	81.25	18.75	85	84.35	16.5	3.5
50	70	30	85	84.35	47.8	2.2
80	25	75	85	84.35	79.1	0.9

Large errors such as these are therefore possible, particularly where low percentages of the acid being determined are present in the sample. They are, however, greatly reduced by more careful selection of the constant used.

Effect of Neutral Fat in Sample

The effect of the presence of neutral fat in the sample analyzed may be judged from the melting-point depressions caused by pure triglycerides in palmitic and stearic acids. Table V gives the results of such measurements for three pure glycerides, samples of which were made available through the courtesy of C. G. King of the University of Pittsburgh Chemistry Department.

Table V. Melting-Point Depressions Caused by Neutral Fat

Fat (Solute)	Weight Acid *Gram*	Weight Fat *Gram*	Per Cent Solute: Weight per cent	Per Cent Solute: Mole per cent	Melting Point ° *C.*	Depression ° *C.*	Depression per 10 Per Cent K_w	Depression per 10 Per Cent K_m
in palmitic acid (melting point 61.93°)								
Trimyristin	0.8332	0.1445	14.79	5.80	60.93	1.00	0.68	1.72
	0.8577	0.1601	15.73	6.22	60.78	1.15	0.73	1.85
Tristearin	0.8616	0.1515	14.95	4.81	60.96	0.97	0.65	2.01
	0.9139	0.1466	13.81	4.41	61.08	0.85	0.61	1.93
Palmito-di-myristin	0.8496	0.1384	14.00	5.26	60.93	1.00	0.71	1.90
	0.6368	0.0945	12.92	4.83	61.03	0.90	0.70	1.86
							Average	1.88
in stearic acid (melting point 69.21°)								
Trimyristin	0.8623	0.1402	13.98	6.00	68.29	0.92	0.66	1.53
	0.8838	0.1506	14.53	6.26	68.19	1.02	0.70	1.63
Tristearin	0.8807	0.1384	13.59	4.78	68.49	0.72	0.53	1.51
	0.8585	0.1537	15.17	5.40	68.33	0.88	0.58	1.63
Palmito-di-myristin	0.8313	0.1099	11.69	4.77	68.39	0.82	0.70	1.72
	0.8655	0.1536	15.08	6.31	68.19	1.02	0.68	1.62
							Averags	1.61

The molar depression constants here obtained for palmitic and stearic acids are approximately the same as those found when using fatty acids as solutes. Agreement among the present results is less close because the molar percentages of

solute present in the mixtures made up, and consequently the total depressions observed, were in all cases small. It is apparent, however, that, as compared with the effect of an equal weight of free fatty acids, neutral fat causes only three- or four-tenths as much depression of the melting point,

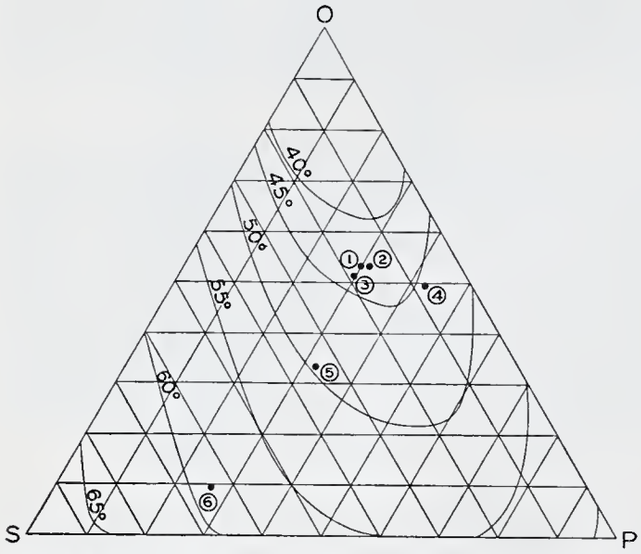

FIGURE 3. FATTY ACID COMPOSITION OF TYPICAL STOCK GREASES

In terms of palmitic acid, stearic acid, and oleic acid (plus others) by difference

depending upon the nature of the glyceride or glycerides present. The effect is thus to cause the mixed-melting-point method to give results that are high by a fraction of the amount of the neutral fat present.

APPLICATION TO STUDY OF TECHNICAL MIXTURES

As an example of the application of the mixed-melting-point method to technical fatty acid mixtures, we may consider the results of analyses for palmitic and stearic acids made on samples of the following six raw greases which enter the manufacture of commercial fatty acids: (1) hard grease (tallows), (2) brown grease, (3) garbage grease, (4) palm oil, (5) oleostearin, and (6) hydrogenated cottonseed stearin.

The fatty acids from these stocks were obtained by Twitchell saponification of the fats in 200-pound batches following the regular commercial procedure. They were not distilled.

Titer, free fatty acid, iodine, and thiocyanogen iodine values are given in Table VI, together with the percentages of oleic and linoleic acids calculated from the two latter determinations. The mixed-melting-point data and results are tabulated in Table VII.

The triangular diagram shown in Figure 3 affords a convenient method for recording and comparing the fatty acid compositions of different samples. The total free fatty acids are here expressed in terms of the three components, palmitic acid, stearic acid, and oleic acid (plus others) by difference. The latter value is obtained by converting the percentages of palmitic acid and stearic acid to their equivalent percentages as oleic and subtracting their sum from the total free fatty acid, as oleic, determined by titration. The three components are then expressed as percentages of their total. For the present samples, these conversions are indicated in Table VIII, the last three columns giving the coördinates of the points laid down in Figure 3.

TABLE VI. ANALYSES OF FATTY ACID MIXTURES FROM TYPICAL STOCK GREASES

	Hard Grease	Brown Grease	Garbage Grease	Palm Oil	Oleo-stearin	Cotton-seed Stearin
	1	2	3	4	5	6
Titer, ° C.	42.80	40.10	37.10	43.60	50.30	60.00
Free fatty acids (as oleic), %	97.79	96.16	93.48	99.46	97.88	99.74
Iodine value	47.10	57.10	63.66	53.74	24.64	6.54
Thiocyanogen iodine value	40.46	45.80	47.75	43.54	22.12	6.34
Linoleic acid, %	7.35	12.48	17.56	11.26	2.78	0.23
Oleic acid, %	37.56	38.36	35.40	37.07	21.80	6.81

TABLE VII. MIXED-MELTING-POINT RESULTS, FATTY ACIDS FROM STOCK GREASES

	Mixtures with Palmitic Acid				Mixtures with Stearic Acid			
Stock	Sample %	Melting point ° C.	Depression ° C.	Palmitic %	Sample %	Melting point ° C.	Depression ° C.	Stearic %
1	16.03	60.52	1.88	29.7	16.01	67.09	2.23	16.6
	18.01	60.22	2.18	27.3	18.00	66.77	2.55	15.2
				28.5				15.9
2	16.01	60.51	1.89	29.1	15.99	67.03	2.29	14.3
	17.98	60.31	2.09	30.2	17.95	66.77	2.55	14.9
	13.96	60.72	1.68	27.7	19.97	66.47	2.85	14.5
				29.0				14.6
3	8.99	61.33	1.07	28.5	9.98	67.99	1.33	20.2
	10.99	61.06	1.34	26.8	11.06	67.79	1.53	17.2
	12.98	60.83	1.57	27.3	11.98	67.61	1.71	14.5
				27.5				17.3
4	17.98	60.63	1.77	40.9	15.01	66.98	2.34	7.4
	20.01	60.42	1.98	40.6	16.96	66.68	2.64	7.6
				40.7				7.5
5	17.95	60.34	2.06	31.1	20.00	67.09	2.23	33.9
	20.01	60.07	2.33	30.1	22.01	66.78	2.54	31.5
				30.6				32.7
6	19.97	59.99	2.41	27.5	22.04	67.88	1.44	62.0
	22.01	59.61	2.79	23.9	24.05	67.78	1.54	62.8
				25.7				62.4

In addition to the ruled coördinates the triangular diagram carries constant-temperature curves showing the solidifying points of ternary mixtures of palmitic, stearic, and oleic acids, drawn according to the data of Carlinfanti and Levi-Malvano (*4*). As pointed out by Lapworth and Pearson (*6*), the oleic acid used by these experimenters could not have been of high purity, so that the position of these curves can only be considered roughly approximate. However, if the samples analyzed and plotted on the triangular diagram actually contained, in addition to palmitic and stearic acids, only oleic acid, their positions with relation to the constant-temperature lines should agree at least approximately with their titers.

The close agreement, in solid acid content, between stocks 1, 2, and 3 is of particular interest. They are identical within the limits of measurement by the mixed-melting-point method, yet in general character and behavior in the plant these stocks are widely different. It will be seen that, if their titers and iodine values are compared with the values that would be expected according to Figure 3, stock 1 appears to be about properly placed, but stocks 2 and 3, having

TABLE VIII. COMPARISON OF FATTY-ACID CONSTITUENTS OF SIX STOCK GREASES

No.	Per Cent Palmitic	Per Cent Stearic	Equivalent Per Cent as Oleic		Per Cent Free Fatty Acid as Oleic	Per Cent Oleic (+ Others) by Difference	Total Fatty Acids	Percentage Composition of Total Fatty Acids		
	P	S	p	s	f	$O = f - p - s$	$T = P + S + O$	P/T	S/T	O/T
1	28.5	15.9	31.4	15.8	97.8	50.6	95.0	30.0	16.7	53.3
2	29.0	14.6	31.9	14.5	96.2	49.8	93.4	31.1	15.6	53.3
3	27.5	17.3	29.2	17.2	93.5	47.1	91.9	29.9	18.8	51.3
4	40.7	7.5	44.9	7.4	99.5	47.2	95.4	42.7	7.8	49.5
5	30.6	32.7	33.7	32.5	97.9	31.7	95.0	32.2	34.4	33.4
6	25.7	62.4	28.3	62.0	99.7	9.4	97.5	26.4	64.0	9.6

higher iodine values and lower titers, call for positions nearer the vertex O. The explanation, of course, lies in the presence of a considerable percentage of linoleic acid in the liquid acids of these stocks. The effect of linoleic acid on the shape of the titer surface, of which the constant-temperature lines represent projected contours, has been discussed in Part I of this series (*13*). The position of stock 4 also reflects an appreciable linoleic acid content.

The composition of any mixture of these stocks can be determined graphically on the diagram. Differences in behavior among such mixtures can thus be considered in relation to specific differences in fatty acid composition.

The usefulness of this type of data in the study of plant processes in the fatty acid industries will be readily apparent.

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Examination of the Phenols of a Low-Temperature Coal Tar

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The commercial utilization of low-temperature tar would remove one of the chief obstacles to the establishment of low-temperature carbonization processes in this country. This primary tar is a unique source of high-boiling phenols, concerning whose chemical structure there has been considerable conjecture but little data.

More exact knowledge of the constitution of these phenols would serve to indicate those industrial markets in which they might be utilized as a new raw material. It is now shown that the fraction of these tar acids boiling up to 260° C. consists of homologs of phenol in which the alkyl groups are largely in a meta position to the hydroxyl group. The methods used in separating individual phenols from groups of isomers are presented and two of the phenols are identified as mesitol and 3-methyl-5-ethylphenol.

The large proportion of high-boiling constituents is a well-known characteristic of low-temperature tar, particularly of the phenolic portion of the distilled tars. Thus the outstanding point of difference between high-temperature or coke-oven tar phenols and the phenols of low-temperature tar is the relative proportion of low- and medium-boiling constituents, as shown in Table I.

Table I. Composition of Coke-Oven and Primary Tar Phenols

	180–210° C.	210–225° C.	225–280° C.	280–320° C.	Pitch
	%	%	%	%	%
Coke-oven tar phenols	60	15	10	7	8
Primary tar phenols	9	24	22	15	30

Although the phenols above the xylenol range form approximately 66 per cent of the tar acids of low-temperature tar, no exact knowledge of their constitution or structure is available. The phenols up to and including the xylenol range have been studied by many investigators, but fractions above 225° C. have received little attention.

Gluud and Breuer (*3*) made cresoxyacetic acid derivatives of a fraction boiling from 237° to 241° C. and from the analyses showed that the phenol approximated the formula $C_9H_{12}O$ which they considered indicated trimethylphenol. Avenarius (*1*), however, from consideration of analyses of allophanic acid derivatives concluded that the low hydrogen content indicated presence of unsaturated side chains in this series, as did Weindel (*11*) who made analyses of the acetyl esters. Steinkopf and Höpner (*8*) stated that some of the phenols above the cresols evidently contained side chains longer than the methyl.

Morgan and Soule (*6*) carefully fractionated the whole range of phenols from both a low-temperature tar and a coke-oven tar and plotted curves of specific gravities versus the mean boiling points of the respective fractions. These curves (Figure 1) show a well-defined minimum point and also indicate that the Carbocoal tar phenols are lower in density than the corresponding fractions of coke-oven tar over almost the entire range. Regarding these curves, Morgan and Soule state: "The decrease in specific gravity of the phenols as the boiling point increases indicates the presence of aliphatic side chains of lower density attached to the phenol nucleus—e. g., cresols and xylenols. In the higher homologs a sharp rise in density and a notable increase in the viscosity of the fractions mark the appearance of α- and β-naphthols in the high-temperature phenols, and bicyclic compounds at least in the low-temperature phenols."

Preparation of Fractions

In the present investigation the phenols boiling from 220° to 260° C. have been examined, particularly to determine the changes in composition responsible for the shape of the specific gravity–boiling point curve as noted by Morgan and Soule (*6*)—i. e., the inflection point—and the appreciable differences in density of corresponding fractions of the

phenols of high- and low-temperature tar. The tar acids studied were obtained from a low-temperature tar produced during some large-scale tests on the Doherty complete gasification process at Toledo, Ohio, May to November, 1925. This tar is usually known as Hydrogas tar.

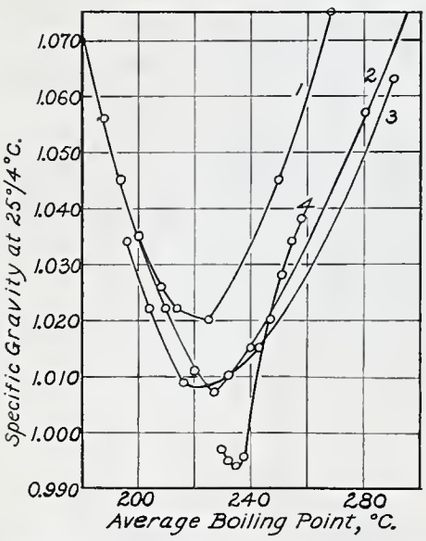


FIGURE 1. BOILING POINT *vs.* SPECIFIC GRAVITY OF FRACTIONS OF PHENOLS FROM VARIOUS TARS

1. Coke-oven tar phenols (Morgan and Soule)
2. Carbocoal tar phenols (Morgan and Soule)
3. Hydrogas tar phenols (Morgan and Meighan)
4. Low-temperature tar phenols (present investigation)

The crude primary tar was distilled from a 1000-gallon (3785-liter) still to a pitch residue of 71° C. melting point, and the phenols were extracted from 1464 gallons (5541 liters) of distillate with caustic soda, care being taken to eliminate hydrocarbon oils from the phenolate solution by agitation with benzene followed by steam distillation. In order to split up the whole range of tar acids into smaller fractions, the acids were fractionally distilled under reduced pressure using a 50-gallon (189-liter) iron still with a fractionating column, 6 feet (180 cm.) long and 6 inches (15 cm.) in diameter, filled with 1-inch (2.5-cm.) Raschig rings. During the distillation the pressure averaged 53 mm.

TABLE II. ANALYSIS OF TAR

Sp. gr. at 25/25° C.	1.03
"Free carbon"	0.71%
Distillation end point at 50 per cent off by volume	330° C.
Pitch melting point (cube-in-water) at 50 per cent off by volume	40° C.
Sp. gr. of distillate at 25/25° C.	0.96
Tar acid content of distillate	21.6%
Nitrogen bases in distillate	3.0%
Sp. gr. of neutral oil at 25/25° C.	0.91
Sulfonation residue, per cent of neutral oil	30.0

Great attention was paid to efficient fractionation, without which the separation by distillation of even fairly simple mixtures is valueless and misleading. After several tests a fractionating column was finally designed that gave excellent results. This was a modification of the column described by Peters and Baker (*7*). Using this column at atmospheric pressure, several of the cuts obtained in the large-scale distillation *in vacuo* were subjected to repeated fractionations. In the first fractionation, two 15° cuts were separated. The first, boiling at 225° to 240° C., was selected because it contained the phenol corresponding to the minimum point of the specific gravity–boiling point curve, while the fraction boiling at 240° to 255° C. was taken as being well up on the rising part of this curve and hence in the range in which clues might be found to account for the difference in density of corresponding fractions of high- and low-temperature tar phenols. During the succeeding fractionations the cuts were made narrower and narrower, until in the sixth and final distillation of the original 225° to 240° C. cut 0.5° cuts were taken, as was also the case in the fifth and last fractionation of the 240° to 255° C. portion. The largest fraction obtained boiled at 234° to 234.5° C., which coincides with the point of minimum density, so that this fraction was used for the attempt to isolate individual compounds and to study their chemical structures.

That the fractionation of the tar acids used in this work was fairly efficient is evidenced by the fact that the specific gravity–boiling point curve (Figure 2) shows to a slight extent the irregularities obtainable by splitting a complete set of isomers into its constituents or into several groups of constituents.

During each fractionation of the two 15° cuts, "spot cuts," consisting of a few drops each, were taken at close intervals for the determination of refractive indices. The curves obtained by plotting these data assisted in following the progress in separation made by each fractionation, and the curves for the final fractionations are shown in Figure 2 together with a curve of specific gravities of the individual cuts. It will be observed that both the refractive index and the specific gravity curves show distinct minima, as in the curve of Morgan and Soule. This point of inflection was considered by Curtis and Beekhuis (*2*) to indicate the appearance above that point of dihydric phenols in appreciable quantity.

CHARACTERISTICS STUDIED

DEHYDROGENATION AND DEOXYGENATION. Partial hydrogenation of the nucleus is one of the possible differences of structure that might account for the observation of Morgan and Soule that phenols of low-temperature tar have lower densities than phenols of the same boiling point from high-temperature tar. In order to test this point, several fractions between 250° and 260° C. were passed over a nickel-thoria catalyst at 350° C. The gas liberated was negligible, whereas with tetrahydronaphthol and tetrahydronaphthalene almost theoretical yields of hydrogen were obtained, together with naphthol in one case and naphthalene in the other. This excludes the possibility of the presence of polynuclear phenols, since the naphthols themselves boil above 280° C., whereas the failure to liberate hydrogen rules out the hydrogenated naphthols.

By deoxygenation the parent hydrocarbon can be obtained. An active carbon catalyst in the presence of hydrogen was found to give better results and at a lower temperature than the classical zinc-dust method of Baeyer. In each case only small yields of hydrocarbons were obtained and these were mixtures of a number of compounds as indicated by the wide boiling range, so that no definite conclusions could be drawn from these tests.

SOLID DERIVATIVES. Attempts were then made to prepare various solid derivatives in order to characterize the phenols more definitely and to aid in the separation of isomers by fractional crystallization. The phenoxyacetic acids, by reaction of the phenols with chloroacetic acid, had been employed by Gluud and Breuer (*3*) in the identification of the lower-boiling phenols of low-temperature tar and had later been applied by Steinkopf and Höpner (*8*) to the xylenols. However, when this method was used with the higher-boiling liquid fractions of tar acids being studied in the present investigation, the reactions were violent and the products consisted largely of noncrystallizable oils. Much more satisfactory results were had with the preparation of the phenylurethans and naphthylurethans, which were also employed by Steinkopf and Höpner. Molecular weight determinations and ultimate analyses of the urethans indicated that the fraction boiling at 234° C. could be represented by the formula $C_9H_{12}O$. Bromo derivatives of the 234° C. fraction were obtained in crystalline form and on analysis confirmed the formula $C_9H_{12}O$ for this cut.

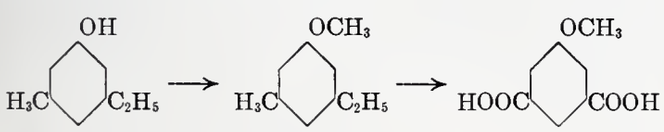
Molecular Weights of Fractions. The molecular weights of the phenol fractions were determined indirectly by the cryoscopic method using the methyl ether of the phenol in benzene solution. This method was found to be more reliable and accurate than the hydrogen equivalent method, using sodium and the toluene solution of the free phenol (*5*). After the third distillation the molecular weights of all of the 5° C. fractions were determined. Unusually high values obtained for the fraction 220° to 225° C., which is in the xylenol range, showed that a large percentage of phenols of molecular weight higher than 122 must be present in this fraction. This fraction was therefore examined more thoroughly and the trimethylphenol, mesitol, separated from the xylenols by the method given below.

Separation by Fractional Liberation and Extraction. The degree of hydrolysis of the sodium salt of a phenol in aqueous solution, and the partition of the phenol itself between two solvents, such as ether and water, are known to be functions of the chemical constitution of the phenol considered. Fractional precipitation by successive addition of small portions of acid to the sodium phenolates has been applied to the separation of phenols, cresols, and xylenols by previous workers. Vavon and Zaharia (*9*) examined various synthetic phenols and found that all phenols could be extracted by ether from the aqueous solution of their sodium salts. The percentage of phenol that was extracted by the ether varied greatly according to the constitution of the phenol. Notably many ortho and diortho compounds were almost completely extracted by the ether in one extraction, demonstrating the high degree of hydrolysis of their sodium salts. A more recent paper on the use of this method presents quantitative data for a number of phenols and indicates commercial possibilities (*4*).

A method of separation combining fractional precipitation and extraction by ether of the phenols from their sodium salts was used in the examination of the phenols boiling over the range 220° to 225° C., proving them to consist of a mixture of mesitol and xylenols. The mesitol was identified by preparation of the dibromide, and by mixed melting point of this with a synthetic specimen of mesitol dibromide.

Oxidation of Side Chains. Although the fractions examined evidently consisted of homologs of phenol, the number, position, and length of the alkyl side chains were yet to be determined, with the evidence strongly in favor of a single long side chain for the 234° C. fraction, since it occurred at the inflection point of the specific gravity and refractive index curves. For this determination, recourse was had to conversion of the alkyl groups into carboxyl groups.

The fraction boiling at 234° C. was in this way converted to a dicarboxymethoxy derivative whose identity with 1-methoxy-3,5-dicarboxybenzene was proved by a mixed-melting-point determination with a sample of this acid obtained synthetically from another source. Since the original tar acid has been shown by several different methods to consist largely of a phenol having the formula $C_9H_{12}O$, the latter must be *m*-methylethylphenol.



The fractions above the 234° C. cut were found to be much more resistant to oxidation with alkaline permanganate, which observation would cast doubt on the existence of either long side chains or unsaturated side chains on the nucleus of these higher boiling phenols.

Probable Composition of Tar Acids 235° to 260° C.

Every test that has been applied to the fractions of these low-temperature tar acids up to 260° C. has failed to show any structural differentiation between them and the corresponding fractions of tar acids from high-temperature tar. A series of cuts of the high-temperature tar phenols were prepared for this comparison from a 10-gallon (37.85-liter) sample of "carbolic tar"—the still residue of coke-oven tar phenols after removal of the cresols and xylenols—which was obtained through the courtesy of the Barrett Company. But nevertheless there remain to be explained the marked differences in physical properties, in the density and refractive index.

A rather simple explanation to account for the relatively low density of the primary tar phenols occurs to the authors. This consists, in brief, in the supposition that in each group of phenol homologs the isomers which predominate in the low-temperature tar acids are those having the alkyl side chains meta or para to each other, while in the high-temperature tar acids an ortho grouping of the same alkyl chains predominates. Examination in the literature of the only group of aromatic homologs for which fairly complete density figures are available, the polymethylated benzenes, reveals rather strikingly the effect of the ortho grouping of side chains in elevating the densities, as shown in Table III, taken from International Critical Tables, and in Figure 3.

Table III. Density Figures

Hydrocarbon	Boiling Point ° C.	d_4^{20}	n_D^{20}
Benzene	80	0.878	1.5014
Toluene	110	0.866	1.4962
o-Xylene	144	0.879	1.5058
m-Xylene	139	0.865	1.4973
p-Xylene	138	0.861	1.4956
1,2,3,-trimethylbenzene	176.5	0.895	1.5132
1,2,4-trimethylbenzene	170	0.870	1.5051
1,3,5-trimethylbenzene	165	0.863	1.4967
1,2,3,4-tetramethylbenzene	204	0.901	1.5187
1,2,3,5-tetramethylbenzene	197	0.894	....
1,2,4,5-tetramethylbenzene	193	0.888	....

It is worthy of note in this connection that the largest 0.5° fraction that was obtained in the fractionation of the low-temperature tar phenols, that boiling from 234° to 234.5° C., was found to consist largely of 3-methyl-5-ethylphenol—i. e., the alkyl groups were in a meta position to one another, while the phenol of $C_9H_{12}O$ formula which was isolated from the 218° to 220° C. fraction was mesitol, in which the three methyl groups are again in a meta grouping.

Of course, the above evidence is entirely too fragmentary to make the proposition anything more than mere conjecture, nor are there sufficient data on the pyrolytic behavior of these phenols to enable one to predict whether the homologs with the alkyl side chains in ortho position to each other would be more stable and hence would be likely to remain in high-temperature tar, whereas the others would be, to a greater extent, destroyed. It is hoped, however, that future workers in this field may devote further attention to this question, and it is suggested that the fractional liberation of the phenols from their phenolate solutions, together with the oxidation of their ethers, offers a convenient method of separating and identifying the isomers.

Fractionation of Tar Acids

The fractionating column used was 1.65 meters long, 12 mm. internal diameter, and packed with 5 × 5 mm. glass Raschig rings. It was connected to the flask by a ground-glass joint and the whole apparatus was made of Pyrex glass. An air condenser or dephlegmator at the top of the column maintained an adequate reflux ratio (approximately 15 to 1). To prevent heat loss the column was surrounded by a close-

fitting concentric glass tube wound with nichrome ribbon which was heated electrically, and the whole assembly was jacketed to avoid drafts.

From the tar acids which had been distilled on a larger scale under reduced pressure, two large fractions were collected over the ranges 225° to 240° C. and 240° to 255° C. These were each separately fractionated at atmospheric pressure, cuts being taken at progressively smaller intervals. The results for the sixth fractionation of acids boiling 225° to

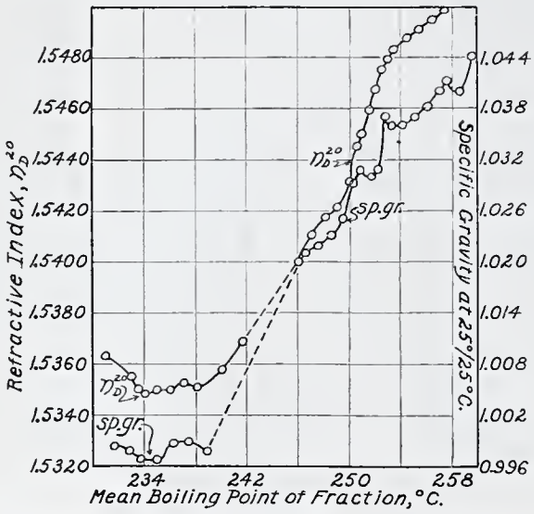


Figure 2. Refractive Index and Specific Gravity of Fractions after Last Fractionation

240° C. are shown in Figure 2. The largest fraction, boiling at 234° C., was selected for particular examination. The fractionation of acids of boiling range 240° to 255° C. was not carried beyond the fifth distillation (Figure 2).

Fraction 220° to 225° C.

Methylation. Samples of the 5° C. cuts obtained after the third distillation of the xylenol range of tar acids were dissolved in an excess of 10 per cent sodium hydroxide solution and converted to their methyl ethers by treatment with dimethyl sulfate. Molecular weights of the ethers were then obtained by the cryoscopic method in benzene.

Table IV. Molecular Weights

Fraction ° C.	Molecular Weight of Phenol
205–215	126
215–220	131
220–225	130
225–230	141
230–235	143
235–240	149

Separation by Fractional Liberation from Phenolates. A sample of 185 grams of phenols boiling from 220° to 225° C. was dissolved in the equivalent amount, 500 cc., of 10 per cent caustic soda solution. This alkaline solution was twice treated with 50 cc. of ether, shaking thoroughly in a separatory funnel for each extraction (extract 1). Then 65 cc. of 2.5 *N* hydrochloric acid were added, 15 cc. at a time, shaking after each addition. The precipitated phenol was extracted with 100 cc. of ether. Another 65-cc. portion of the acid was similarly added, followed by shaking with ether, etc. In all, 500 cc. of acid were added, making 8 extractions. The ethereal extracts were washed with dilute acid, then with water, and after drying over anhydrous sodium sulfate the ether was removed on the water bath. The phenol portions were distilled at 15 mm. pressure.

Table V shows the degree of separation of compounds that was obtained.

The molecular weights were determined by the cryoscopic method, using the methyl ether of the phenol with benzene as solvent. Of known phenols of molecular weight 136 boiling within the range 215° to 225° C. the following are described: mesitol (2,4,6-trimethylphenol), boiling point 220° C.; 2-methyl-5-ethylphenol, boiling point 220° C.; and 2-ethyl-5-methylphenol, boiling point 226° C.

Mesitol, being substituted in both ortho positions to the hydroxyl group, would be less acid than the xylenols present and therefore would be expected in the first fractions. Fraction 1 was therefore redistilled at atmospheric pressure and that part boiling between 218° and 220° C. was taken for examination.

Bromides. A portion (5 grams) of the phenols boiling at 218° to 220° C. was brominated in the cold, in chloroform solution, by addition of one molecular equivalent of bromine. The monobromide was distilled under reduced pressure after removal of the solvent. Since no solid product could be obtained, a second molecule of bromine was added. On cooling, a crystalline solid (4 grams) separated from the chloroform solution. After recrystallization it had a melting point of 159° to 160° C. Analysis showed this to be a dibromide, $C_9H_{10}OBr_2$.

Calculated for $C_9H_{10}OBr_2$: Br, 54.33. Found: Br, 54.2.

Dibromomesitol is described as having a melting point of 159° to 160° C. The melting point of a mixture of the above dibromide with an authentic specimen of 3,5-dibromomesitol was unchanged. In this way the identity of the above dibromide was established and the presence of mesitol in the tar acids boiling at 220° C. confirmed. The residual liquid bromide was not examined further.

Table V. Separation of Compounds

Fraction	Weight	n_D^{20}	Molecular Weight
	Grams		
1	35	1.5335	133.5
2	25	1.5350	132
3	25	1.5350	134
4	25	1.5360	129
5	25	1.5360	127
6	20	1.5360	127
7	20	1.5380	126
8	10	1.5380	125

Methyl Ether. The methyl ether of the phenol boiling at 218° to 220° C. was prepared by treatment at 30° C. of an alkaline solution of the phenol with dimethyl sulfate. This ether had a boiling point of 203° C., and molecular weight of 147 by the cryoscopic method in benzene. $C_9H_{11}OCH_3$ requires a molecular weight of 150.

Fraction 234.0° to 234.5° C.

This was the largest 0.5° cut obtained after the sixth fractionation of the original fraction, 225° to 240° C.

Calculated for $C_9H_{12}O$: C, 79.4; H, 8.82. Found: C, 79.98; H, 9.00.

Phenylurethan. The method found to be best applicable for the preparation of the phenylurethan of this phenol fraction was that described by Wehuizen (*10*), who recommended carrying out the reaction in petroleum naphtha (boiling point, 170° to 200° C.) solution, obtained for this work by the fractional distillation of some commercial kerosene. Three grams of the tar acid, 3 grams of phenyl isocyanate (a slight excess over molecular equivalent), and 7 cc. of the petroleum naphtha (170° to 200° C.) were mixed and heated on the water bath for 1 hour.

$$C_6H_5N{:}CO + C_9H_{11}.OH \longrightarrow C_6H_5NH.COOC_9H_{11}$$

After the mixture had been standing at room temperature overnight, the phenylurethan crystallized out. The yield of crude urethan was 2.1 grams, or 36 per cent of the theoretical yield. It was purified by several crystallizations from carbon tetrachloride followed by one from ligroin (80° to 100° C.). The melting point was 145° C.

Calculated for $C_{16}H_{17}O_2N$: C, 75.29; H, 6.65; N, 5.49. Found: C, 75.26; H, 6.79; N, 5.63.
Molecular weight, calculated: 255. Found (Rast's camphor method): 249.

NAPHTHYLURETHAN. This was prepared in the same manner as the phenylurethan except that α-naphthyl isocyanate was used. This reagent had the disadvantage of producing dinaphthyl urea which was insoluble in the petroleum ether and had to be separated by fractional crystallization. The melting point of the naphthylurethan was 140° C.

Calculated for $C_{20}H_{19}O_2N$: C, 78.68; H, 6.22; N, 4.59. Found: C, 78.89; H, 6.47; N, 4.59.
Molecular weight, calculated: 305. Found (in camphor): 297.

BROMIDES. Bromides of the phenol fraction were prepared by the slow addition of a chloroform solution of bromine to the phenol, also in chloroform, while cooling with ice water. After standing until the solution was only slightly colored with bromine, the chloroform was removed by a vacuum pump and the liquid residue distilled. The distillate thus obtained crystallized on cooling. By fractional crystallization from petroleum ether (40° to 60° C.) two solid bromides were obtained. A dibromide, which was the more soluble in the petroleum ether, was secured in the form of stout needles and boiled at 160° C. at 5 mm. The melting point was 150° C. A tribromide was obtained (from petroleum ether) as fine needles, melting point 91° C.

Calculated for $C_9H_9OBr_3$: Br, 64.31. Found: Br, 64.00.

A liquid, apparently a monobromide, was also obtained. On treatment with more bromine it yielded a mixture of the above two bromides.

METHYL ETHER. This was prepared by treating the sodium salt of the phenol fraction in alkaline solution with dimethyl sulfate at 40° to 50° C. The yield was almost theoretical. In benzene solution it gave excellent results for the determination of molecular weight by the cryoscopic method, unlike the phenols themselves which are highly associated in benzene.

This ether was a colorless liquid of pleasant odor and did not darken on standing. It had a boiling point of 83° to 85° C. at 12 mm.

Molecular weight, calculated for $C_9H_{12}O + CH_2$: 150. Found: 150.

OXIDATION OF ETHER. The ether was suspended in a small amount of 5 per cent sodium hydroxide solution, and boiling 5 per cent potassium permanganate solution was run in dropwise with vigorous stirring, while the reaction liquid was kept boiling. Sufficient permanganate was added to oxidize all side chains to carboxyl groups, but apparently because of side reactions, much more than theoretical was required to get a fair yield of acid. The methoxy acids when formed were quite stable. Addition of 1 liter of the potassium permanganate solution usually required 2 to 3 hours. The supernatant liquid was then generally colorless. Unchanged ether was removed by steam distillation and the solution then separated from the manganese dioxide by filtration. The manganese dioxide was twice treated with 5 per cent sodium hydroxide solution and the washings were added to the main filtrate which was then evaporated to small bulk on the water bath. On acidifying the cold concentrated aqueous solution, the organic acid was liberated and filtered off. The aqueous liquor was shaken with ether to recover the last traces of the acid product of oxidation. This gave a total yield of 43 per cent of the theoretical of crude acid which was recrystallized from acetone and benzene as flat prisms, or from water as very fine needles, melting point 275° C.

Calculated for $C_6H_3(OCH_3)(COOH)_2$: C, 55.09; H, 4.11; OCH_3, 15.81. Found: C, 55.39, 55.27: H, 4.12, 4.20; OCH_3, 15.85, 15.73.

A smaller amount of an acid, melting point 238° C., was also isolated in this oxidation and was shown to be identical with the acid obtained on the oxidation of the ether of tar acid fraction 250° to 251° C. No other acids were isolated. A small amount of sirupy residue on further oxidation gave the acid of melting point 275° C.

SYNTHESIS OF 5-METHOXY-1,3-DICARBOXYBENZENE. The starting material for this synthesis was a sample of 150 grams of 4-amino-1,3-dimethylbenzene obtained from the Eastman Kodak Company. In brief, the steps consisted of a nitration of the acetylated amine for introduction of the nitro group into the 5-position, diazotization of the amino group and replacement with H, reduction of the nitro group to the amino, diazotization of the latter, and conversion to the hydroxyl. (Since the completion of this work, the 5-amino-1,3-dimethylbenzene has been made available by the Eastman Kodak Company, greatly simplifying the above operations.) The yield of the 5-hydroxy-1,3-dimethylbenzene was only 5 grams, or 3.3 per cent of the theoretical after all these operations. This product was then methylated and oxidized with alkaline permanganate as described above. After several crystallizations from 15 per cent alcohol, the dicarboxy acid was obtained as fine needles with a melting point of 275° C. The melting point of the methoxydicarboxybenzene obtained from the tar acid fraction boiling at 234.5° C. had a melting point of 275° C. and a mixed melting point of the two was 274° C.

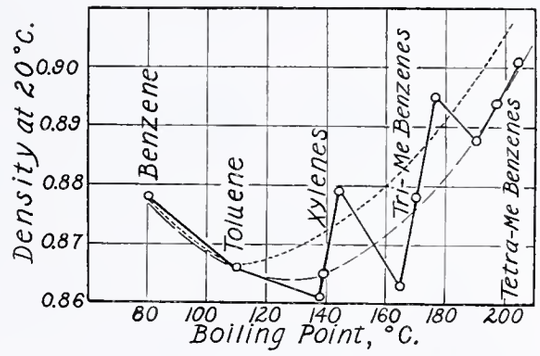


FIGURE 3. DENSITIES OF BENZENE HOMOLOGS, WITH TWO HYPOTHETICAL CURVES

Upper curve, mixture rich in ortho homologs
Lower curve, mixture poor in ortho homologs

FRACTION 250.5° TO 251° C.

This was the largest 0.5° cut obtained after the fifth distillation of the original fraction 240° to 255° C. The analyses for carbon and hydrogen content of the phenol as well as of the phenylurethan suggested a mixture of phenols, $C_9H_{12}O$ and $C_{10}H_{14}O$. No solid bromides could be obtained from this fraction of phenols.

METHYL ETHER. This was prepared as described above and gave a liquid boiling at 96° to 98° C. at 12 mm., with a pleasant odor and slightly yellow color which did not darken on standing. The molecular weight, calculated for $C_{10}H_{14}O + CH_2$ was 164; found (in benzene), 158. This suggests that this fraction is probably a mixture of phenols $C_9H_{12}O$ and $C_{10}H_{14}O$.

SUMMARY

Low-temperature tar phenols over the range 220° to 260° C. have been carefully fractionated and examined, and the fraction boiling around 220° C. shown to contain mesitol. The fraction of minimum density, boiling at 234° C., has been shown to consist mainly of 3-methyl-5-ethylphenol.

Crystalline derivatives, bromides, and phenylurethans of mesitol and methylethylphenol are described.

Examination of the fractions of tar acids up to 260° C. has indicated that they consist of mixtures of the simple alkylated homologs of phenol.

A tentative explanation for the uniformly lower densities of fractions of low-temperature tar acids as compared with

corresponding fractions of high-temperature tar acids is offered.

ACKNOWLEDGMENT

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Short-Cut Method of Hydrocarbon Analysis

II. Application to Analysis of Stabilizer Bottoms

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A short-cut method of hydrocarbon analysis applicable to certain types of routine samples has been developed to reduce the time and expense of such analyses. Its application to the analysis of stabilizer gas and reflux has previously been described, and its further application to stabilizer bottoms is described in this paper.

Synthetic samples, covering the range of compositions normally found for stabilizer bottoms, have been made up and run by the short-cut method employing the changes in apparatus and procedure necessary for samples of this type. From the resulting distillation curves, graphs have been prepared by the use of which routine samples of stabilizer bottoms may be analyzed. In the use of these graphs, corrections must be applied for the presence in such samples of certain constituents not present in the synthetic samples, and correction charts for this purpose have been prepared by calculating the effect of these components on the distillation curves.

This method, applied to stabilizer bottoms, checks microfractionation analysis within 0.5 per cent on the propane, 1 per cent on the butane, and 2 per cent on the pentane and hexane plus heavier hydrocarbon fractions. It offers distinct advantages from the standpoint of ease of operation and economy in time and materials.

IN VIEW of the fact that control of refinery equipment requires frequent analyses of samples of similar composition, it was felt that a rapid, economical, and accurate method of analysis would be of great value. Such a method, based on a distillation analogous to the Engler distillation for naphthas, was described by Rosen and Robertson (*7*) and is now being used by several laboratories for analyzing stabilizer gas and reflux. In the present paper its application to the analysis of stabilizer bottoms is described.

So-called graphic methods of analysis are limited in application because they are based on physical characteristics of the mixture to be analyzed, and the number of components which can be determined is only one more than the number of determinable physical characteristics. In the short-cut method the analysis is obtained by considering temperatures at different per cents-off on a distillation curve. Thus, for three-component mixtures or mixtures which can be reduced to three components, such as stabilizer gas and reflux, it is necessary to consider temperatures at two different per cents-off, while for four-component systems, or mixtures which can be so treated, such as stabilizer bottoms, it is necessary to employ temperatures at three different per cents-off.

Several graphical methods for the analysis of hydrocarbons and similar mixtures have been described in the literature. Colman and Yoeman (*4*) supplied this principle to the analysis of mixtures of benzene, toluene, and xylene. Methods for the graphical analysis of gasolines and natural gasolines from the A. S. T. M. distillation curve have been described by Smith (*8*), Pocock and Blair (*6*), and Blair and Alden (*1*), and appear to have considerable application for such hydrocarbon mixtures.

Stabilizer bottoms or similar light naphthas consist of propane, butane, pentane, and hexane plus heavier hydrocarbons having compositions varying between the two following extreme type analyses:

TABLE I. WEIGHT PER CENT OF STABILIZER BOTTOMS

SAMPLE	PROPANE	BUTANE	PENTANE	HEXANE PLUS HEAVIER HYDROCARBONS
1	3	42	45	10
2	0	22	24	54

The analysis of samples of this type by the short-cut method necessitated changes in apparatus, changes in procedure, and preparation of curves applicable to the analysis of four-component mixtures covering the above composition range. The method of attack was to develop an apparatus and procedure applicable to this type of sample, to make up synthetic mixtures representing various concentrations of the different components, to run these mixtures by the apparatus, and to prepare the graphical analysis curves from the distillation curves thus obtained.

The propane and butane used in this investigation were the same purified hydrocarbons used in the investigations by

Rosen and Robertson (7). The pentane and hexane were obtained from the fractionation of natural gasoline. Microfractionation analyses showed that these hydrocarbons were not pure, but in making up synthetic mixtures allowance was made for the impurities. The pentane and hexane contained iso-compounds, but no unsaturates.

Apparatus

The apparatus used in this work is shown in Figure 1.

The graduated buret B and the leveling bulb A are for measuring the gases to be used in the preparation of the synthetic mixtures, the gas containers being attached at Q. The distillation bulb C is surrounded by test tube D, while the thermocouple leads E connect the thermocouple resting on the bottom of bulb C to the potentiometer. The open-end manometer F shows the

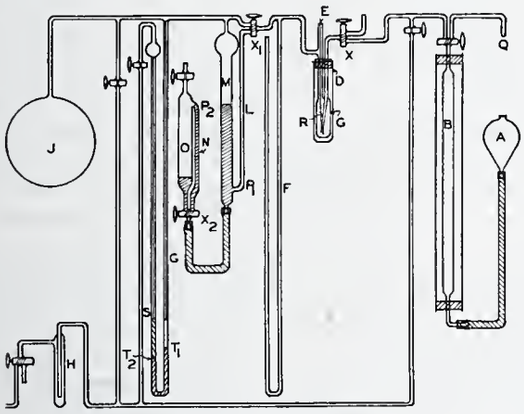

Figure 1. Apparatus for Distilling Liquid Samples

pressures on the distillation bulb C. The tube L, the bubbler M, and the reservoir O are so arranged that any desired pressure may be automatically maintained on the bulb C. The closed-end manometer G is so constructed that the readings are greatly magnified for accurate reading. It is made of 2-mm. tubing with about 12 inches (30 cm.) of the bottom made of 6-mm. tubing, and partly filled with mercury. Above the mercury (point T_2) on the closed side is a light hydrocarbon oil having substantially zero vapor pressure. The manometer is evacuated on the closed side above the oil. In Figure 1 the manometer is represented as it would be if the receiving bulb J were evacuated, the oil in the closed side just reaching up into the small part of the manometer to the point S. Now as pressure builds up in J, as gas is admitted into this receiver, the level T_1 will drop, pushing the oil level up on the other side much more than the drop at T_1. The oil level at S is used as the indication of pressure, and it will move about 4 mm. for each mm. of pressure built up in J, if the manometer is constructed as described.

It is necessary to calibrate the manometer G and since, in the apparatus shown in Figure 1, the volume of J plus the additional volume of lines and free space above the mercury level in M is different at different pressures, owing to the drop in the mercury level in M, this was taken into account in calibrating G, so that at any pressure one division corresponded to a definite volume of gas entering J and was equal to the amount which would build up 1 mm. pressure when the mercury level in M was even with P_2.

The receiving bulb J is of 3-liter capacity. The mercury trap H is placed in the vacuum line.

The arrangement shown at L, M, O is for the purpose of maintaining a constant pressure on J. At the beginning of the run, J, M, and O are evacuated and as the sample in distillation bulb C (Figure 1) gradually builds up pressure (with stopcock X_1 open to L), the mercury in L, which, if there were no pressure in C, would stand even with point P_2, is pushed down toward P_1. Now when, with stopcock X_2 open to N, the pressure in C in mm. of mercury equals the vertical distance between P_1 and P_2, gas will bubble up through the mercury in M and escape into receiver J. As vapor collects in J the pressure therein gradually builds up so that the mercury level in M drops, the excess mercury flowing over at P_2 into reservoir O. Meanwhile the pressure at P_1 does not change, always remaining the vertical distance between P_1 and P_2. At the end of a determination when J is evacuated, stopcock X_2 is opened to O directly and the reservoir raised so that the mercury therein flows back into M. The apparatus is then ready for another determination.

The inner tube R in the distillation bulb C is for the purpose of facilitating the boiling of the sample and was found necessary because of the tendency of the sample to superheat, thus destroying the smoothness of the distillation curve. This tendency was much more marked in the case of stabilizer bottoms than in that of the lighter stabilizer gas and reflux.

It was found necessary to distill stabilizer bottoms at 200 mm. pressure instead of at 760 mm., because at the latter pressure only a small percentage of the sample would distill over below room temperature, and room temperature cannot be exceeded in this type of apparatus without condensation in the lines. Accordingly, the automatic pressure regulator L, M, O was found necessary because at the lower distillation pressure the small variation in pressure, inevitable in manual regulation, corresponded to a much larger temperature change than was the case when the distillation was carried out at atmospheric pressure.

The special manometer G was substituted for the ordinary closed-end manometer to obtain greater accuracy, made necessary by the fact that at 200 mm. pressure a much larger expansion bulb J was necessary for the same size sample than at 760 mm.

This apparatus differs from the original short-cut apparatus in the way heat is supplied to distillation bulb C. Since, in the course of distilling stabilizer bottoms at 200 mm., it is necessary for distillation bulb C to be warmed to approximately room temperature, it was impractical to warm it by exposure to atmospheric temperature as was found satisfactory in the original short-cut procedure. The arrangement adopted was to enclose C in test tube D and surround this with a Dewar flask, filled with acetone cooled down with solid carbon dioxide, in which was inserted an immersion heater.

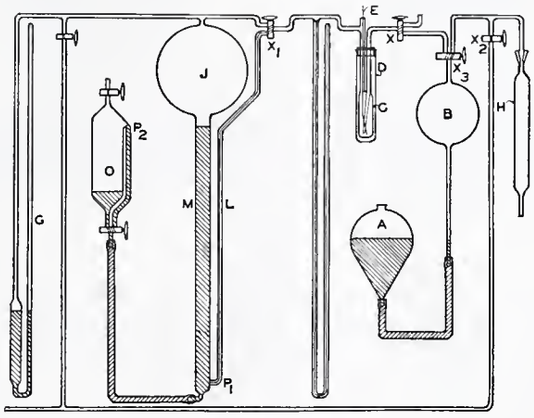

Figure 2. Apparatus for Distilling Either Liquid or Gaseous Samples

It is entirely practical to construct a single apparatus capable of running stabilizer gas, reflux, or bottoms. Figure 2 is the diagram of the apparatus constructed in the laboratory for this purpose.

The measuring bulb B (500 cc. capacity) and drying tube H are provided for measuring and introducing gas samples. The other parts of Figure 2 serve the same purpose as the corresponding parts of Figure 1. For convenience J (3000 cc. capacity) is mounted on top of M (25 mm. inside diameter), while the latter is made more than 760 mm. long, so that with J evacuated the distillation may be carried on at atmospheric pressure, which is the pressure used in the analysis of stabilizer gas and reflux. However, it is not necessary that M be more than 300 or 400 mm. long, since the distillation of stabilizer gas can be started with sufficient pressure in J, which added to the length of M will equal 760 mm. The manometer G is of the closed-end reservoir type, since it was felt that such a manometer would be accurate enough for routine analysis. The volume of bulb C and lines from X to P_1 is about 11 cc.

At the bottom of distillation bulb C is a triple junction copper-constantan thermocouple made of No. 36 B & S wire, the cold

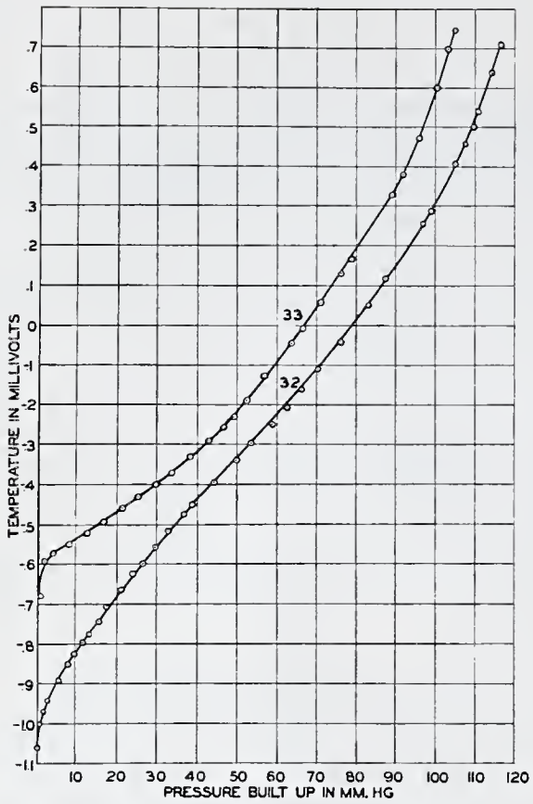

FIGURE 3. TYPICAL DISTILLATION CURVES FOR SYNTHETIC LIQUID SAMPLES

	CURVE 32	CURVE 33
Propane, weight per cent	5.0	0.0
Butane, weight per cent	30.0	30.0
Pentane, weight per cent	43.4	46.6
Hexane, weight per cent	21.6	23.4
Total pressure, mm.	126	112
Millivolts, 10 per cent off	−0.80	−0.50
Millivolts, 40 per cent off	−0.34	−0.26
Millivolts, 70 per cent off	+0.13	+0.18
Temperature, 10 per cent off, ° C.	−21.4	−13.3
Temperature, 40 per cent off, ° C.	−9.0	−6.3
Temperature, 70 per cent off, ° C.	+3.5	+4.7

junction of which is maintained at ice temperature. The millivolt readings are taken on a portable potentiometer reading to tenths of a millivolt. A single-junction thermocouple could be used with a more sensitive potentiometer.

PROCEDURE

The general procedure followed for making up synthetic mixtures was to make up a base stock of pentane and hexane and then to introduce some of this into the distillation bulb C (Figure 1). To this the desired amount of propane and butane was added.

To make the base stocks a glass bulb fitted with a stopcock was evacuated and weighed. A measured amount of hexane was introduced into this bulb and the weight taken; pentane was then introduced and the bulb weighed again. From these weights and the analysis of the pentane and hexane, the exact composition of the base stock was calculated.

Some of this stock was then quantitatively introduced into the distillation bulb of the apparatus through stopcock X. This was done by cooling the bulb C with solid carbon dioxide, inverting the glass bulb containing the base stock, connecting it to stopcock X with rubber tubing, and after opening X (with the lines evacuated), opening the stopcock on the glass bulb slightly; thereby all the base stock coming from the bulb was collected in C, leaving the lines clear. Stopcock X was then closed and the bulb containing the base stock removed and weighed. The weight of the base stock introduced was thus obtained by difference, and from this weight the amount of propane and butane necessary for any desired composition was calculated, measured in B, and added to the sample.

In the course of the work this procedure was used to make up base stocks of various compositions ranging from a pentane-hexane ratio of 0.5 to 2.

After the synthetic mixture was prepared as described above, tube D was placed around C and the whole surrounded with a Dewar flask containing acetone cooled with solid carbon dioxide to below the boiling point of the sample. A 10-ohm heater was placed in the bottom of the Dewar flask, and for a 1-pint (0.473-liter) flask, one ampere of current passed through the heater. The amount of heat was regulated so that the actual distillation was completed in 30 to 40 minutes.

With J, M, and L evacuated, the height of the reservoir O was adjusted to maintain a pressure of 200 mm. on distillation bulb C. When the distillation was started, simultaneous readings were taken on the temperature of the boiling liquid in C and the manometer G, respectively. These readings plotted against one another gave the distillation curve. When the temperature in C approached room temperature, the distillation was stopped by closing stopcock X_1, evacuating J, and opening stopcock X_1 to allow passage of the gas directly from C to J. The additional pressure built up in J was noted. If any liquid remained in C the evacuation was repeated. The total additional pressure built up in J was added to the distillation curve to make up the total pressure built up by the sample. On the basis of the total pressure the temperatures at different per cents-off were determined. Typical synthetic distillation curves are shown in Figure 3.

The procedure for making routine distillations on the apparatus shown in Figure 2 is much the same as that just described.

To analyze a liquid sample, O, J, and C are evacuated and C is surrounded with solid carbon dioxide. The bomb containing the sample is connected with the valve on the underside by means of a short piece of rubber tubing to stopcock X, which is opened to allow evacuation of the line to the valve on the bomb. With X_1 closed the valve on the bomb is opened slightly until about 3 cc. of liquid sample collect in C. The stopcock X is now closed and the sample bomb removed. From this point, the procedure is the same as that described above.

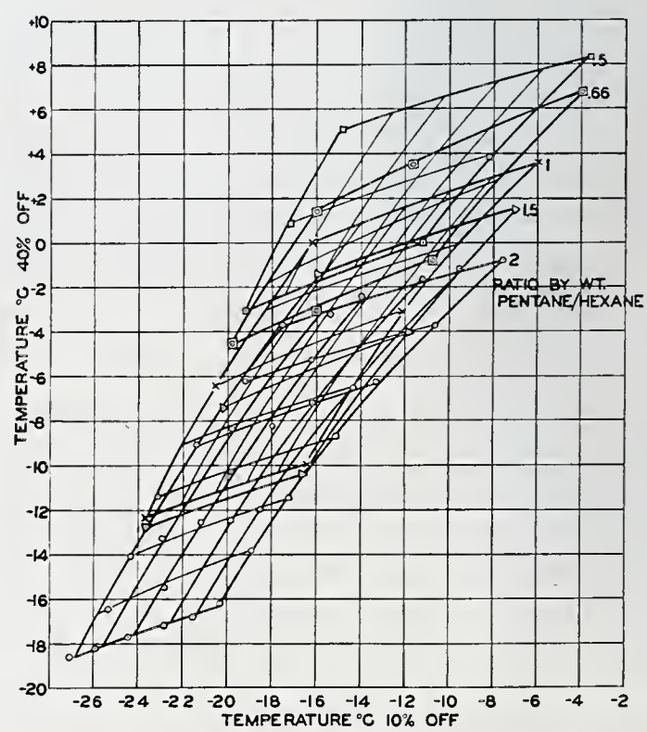

FIGURE 4. 10 AND 40 PER CENT TEMPERATURES FOR ALL SYNTHETIC SAMPLES

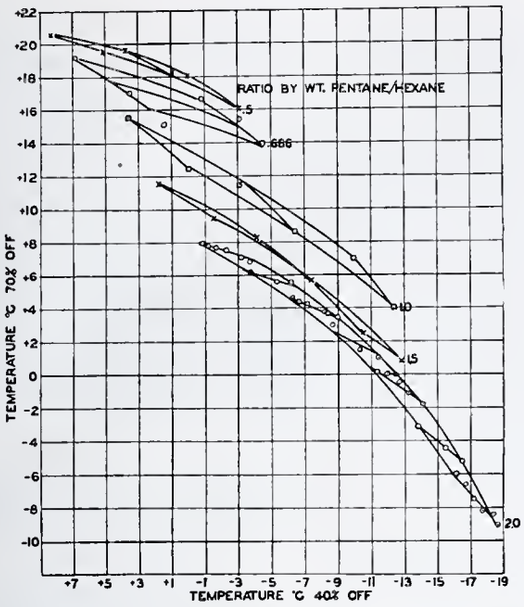

FIGURE 5. 40 AND 70 PER CENT TEMPERATURES FOR ALL SYNTHETIC SAMPLES

The procedure for distilling a gas sample is the same as that described by Rosen and Robertson (7) except that a few minor changes are made necessary by the automatic pressure regulator. In addition, just before beginning the distillation it is believed preferable to measure the fixed gases and methane over into J by opening X_1 directly to J, rather than to pump directly from C as described in the above paper.

PREPARING GRAPHS

As previously explained, it is necessary to consider temperatures at three different per cents-off in order to form a basis for the analysis of four-component mixtures. There still remains the problem of choosing the best three per cents-off and the best method of plotting these temperatures obtained from runs on synthetic mixtures.

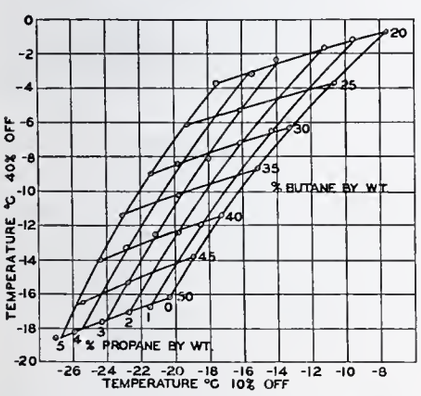

FIGURE 6. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 2

EXTRAPOLATION DATA

Pentane-hexane	Correction 10% ° C.	Correction 40% ° C.
1.8	+0.3	+0.8
1.9	+0.2	+0.4
2.0	0.0	0.0

In this work the temperatures at 10, 40, and 70 per cent have been chosen as being the most feasible. The 10 per cent point was chosen because it is as near the beginning of the distillation as it is safe to assume that the unevenness due to slight superheating and other irregularities incident to starting the distillation have been smoothed out. The 70 per cent point is as near the end of the curve as it is practical to take, since with heavy samples the 70 per cent point may be near or past the end of the curve. The 40 per cent point was chosen because it is approximately half-way between the other two and apparently gave as good graphs as any other point. In addition to the above considerations, these three per cents-off gave graphs which permitted the greatest accuracy in the determination of propane.

The method adopted was to prepare graphs representing plane sections of a solid figure, thus limiting each graph to temperatures at two per cents-off. Figure 4 shows all the 10 and 40 per cent temperatures plotted against each other for all the synthetic samples, while Figure 5 shows all the 40 and 70 per cent points similarly plotted. The lines in each system of curves on this figure represent constant concentration of propane and butane. Figures 6, 7, 8, 9, and 10 are the curves in Figure 4 plotted separately. Figure 5 could also be divided into several curves, but this was not considered necessary since such a series would not differ greatly.

It is to be noted that the graphs in Figures 6, 7, 8, 9, and 10 each have a corresponding graph in Figure 5 and that all points in each graph represent the samples made up with a base stock having the pentane-hexane ratio given with the graph.

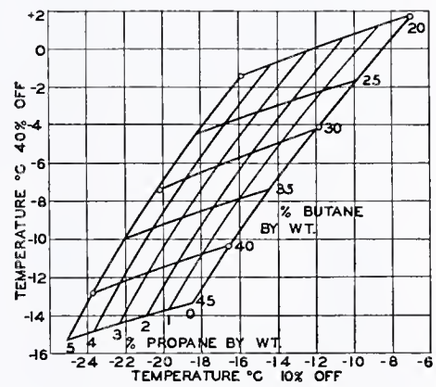

FIGURE 7. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 1.5

EXTRAPOLATION DATA

Pentane-hexane	Correction 10% ° C.	Correction 40% ° C.
1.3	+0.2	+0.4
1.4	+0.1	+0.2
1.5	0.0	0.0
1.6	−0.2	−0.4
1.7	−0.3	−0.8

These graphs are used to analyze unknown samples. The procedure is to plot the 40 and 70 per cent temperatures against one another on Figure 5. These temperatures are plotted first because the corresponding graphs do not intersect as do the 10 to 40 per cent graphs (Figures 4 and 5). This gives a pentane-hexane ratio, and the 10 and 40 per cent-off temperatures are then plotted on the 10 to 40 per cent graph corresponding to this pentane-hexane ratio. For example, if a sample shows 40 and 70 per cent temperatures of −4 and +13.6° C., respectively, these values are plotted on Figure 14 (derived from Figure 5 as described below) and fall on the curve corresponding to a pentane-hexane ratio of 1. This value corresponds to Figure 8 of the 10 to 40 per cent graphs; so this graph is used to obtain the propane and butane concentrations of this sample. The procedure in cases where the 40 and 70 per cent temperatures fall on a curve in Figure 14, for which there is no corresponding 10 to 40 per cent graph, will be described below. The pentane and hexane concentration may be obtained from the following formula:

$$\% \text{ pentane} = \frac{R}{1+R}(100\text{-}P\text{-}B)$$

$$\% \text{ hexane} = \frac{1}{1+R}(100\text{-}P\text{-}B)$$

when R is the pentane hexane ratio, P is the per cent of propane, and B is the per cent of butane.

CORRECTIONS

In analyzing routine samples by the above procedure it was found necessary to correct for the effect of butylene and isobutane on the distillation curves, since only normal butane was used in making up the synthetic mixtures. Graphs giving the corrections for the 10 and 40 per cent points for this effect are shown in Figure 11.

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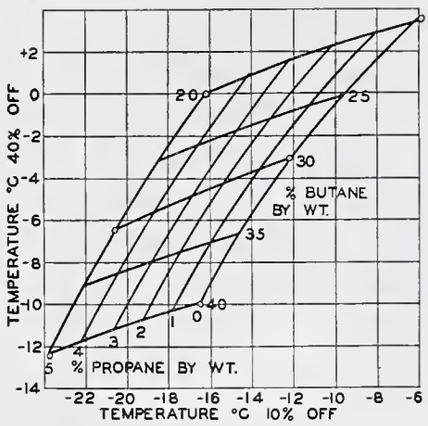

FIGURE 8. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 1

EXTRAPOLATION DATA

Pentane-hexane	Correction 10% ° C.	Correction 40% ° C.
0.832	+0.4	+0.9
0.909	+0.2	+0.5
1.000	0.0	0.0
1.100	−0.1	−0.2
1.200	−0.2	−0.4

These curves were prepared by the calculation of two sets of distillation curves, one for samples containing only normal butane in the butane fraction, and one for samples containing 53 per cent butylene in the butane fraction. This concentration of butylene was used because it gave a butane fraction having an average boiling point of −3.2° C. which was the average boiling point observed for this fraction in routine samples. The calculation of the curves was undertaken to avoid making numerous synthetic runs.

These calculations were carried to the 40 per cent point, so that the correction at 10 and 40 per cent could be obtained. While it is realized that such a calculated curve might not be the same as an experimental one of the same composition, it is felt that, inasmuch as the curves being compared are calculated in the same manner, the butylene would have the same effect on the experimental curves as on those calculated.

The method employed for calculating the distillation curves is based on Murray's formula (*5*) for calculating equilibrium between liquid and vapor hydrocarbon mixtures:

$$C_1 = \frac{LC}{100\frac{P_c}{P} + L\left(1 - \frac{P_c}{P}\right)}$$

where C_1 = liquid moles of any hydrocarbon
L = sum of all liquid moles
C = total moles of a component in the mixture
P_c = vapor pressure of a pure component
P = absolute pressure of the system

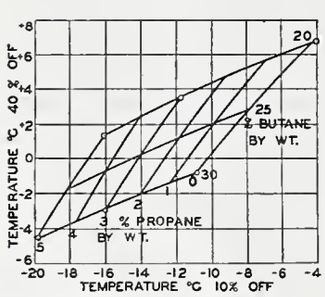

FIGURE 9. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 0.666

EXTRAPOLATION DATA

Pentane-hexane	Correction 10% ° C.	Correction 40% ° C.
0.588	−0.2	−0.7
0.624	−0.1	−0.4
0.666	0.0	0.0
0.714	+0.2	+0.5
0.769	+0.4	+0.9

A graph for the rapid solution of Murray's formula was prepared by Cerini (*2*). This graph, however, was not accurate enough for the purpose desired, since it was designed to take care of all values of L. Accordingly a simplified nomographic chart shown in Figure 15 has been constructed to cover only high values of L.

A distillation was considered as a series of small flash distillations. To calculate a distillation curve, the mole per cent of each component for the original mixture was first calculated, and from this the boiling point of the mixture was determined by assuming a boiling temperature and calculating the vapor pressure of the sample for this temperature. From the vapor pressures at two temperatures near the boiling point, the latter was ascertained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperatures, drawing a straight line through the two points, and noting where it crossed the line corresponding to the pressure of the system. All vapor pressure values for pure compounds were obtained from the chart prepared by Brown and Coats (*3*).

It was now assumed that a temperature rise of 1° or 2° took place and that a certain amount of vapor was distilled off. P_c/P was now calculated for the new temperature, a value of L assumed, and C_1/C obtained for each component from Figure 15. Since C is known, C_1 for each component is thus obtained. These added together should give the value of L assumed; otherwise a new value of L must be assumed and the process repeated. When a value of L is found which will equal the sum of the C_1 values calculated from it, 100-L is taken as the per cent evaporated for the rise in temperature chosen.

The mole per cent for each component is now calculated, being C_1/L for each component. To check the above calculation, the vapor pressure of the partly distilled sample may now be calculated at the new temperature and should equal P. Another rise in temperature is now assumed and the above calculation repeated. Each of these calculations gives a point on the distillation curve, the temperature being plotted against the total mole per cent weathered off.

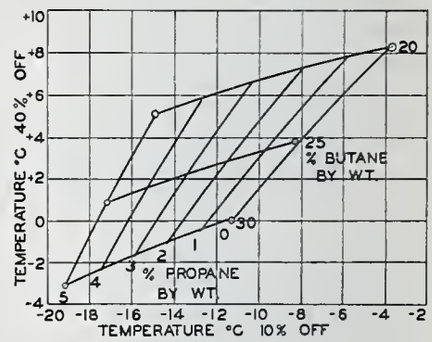

FIGURE 10. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 0.5

EXTRAPOLATION DATA

Pentane-hexane	Correction 10% ° C.	Correction 40% ° C.
0.500	0.0	0.0
0.526	+0.1	+0.4
0.555	+0.2	+0.7

In this work a temperature rise was chosen which would give an L value of about 95, since it was believed that such a value would approximate distillation conditions. The larger the value of L, the more nearly are distillation conditions approached, but the calculation becomes more tedious as the value of L increases.

A comparison of calculated and experimental distillations is shown in Figure 16. The reason that curves A and B diverge is probably that B contains isopentane and isohexane, while the vapor pressure data used for calculating A were for normal hydrocarbons only. Since it was desired to determine the effect of butylene, it was not believed that the curves should necessarily coincide as long as they were similar.

To apply these corrections, the observed 10 and 40 per cent temperatures are plotted on the proper graph and observed propane and butane percentages obtained. These are plotted on Figure 11 to obtain 10 and 40 per cent corrections, which are algebraically added to the original values and the correct propane and butane concentrations obtained from the 10 to 40 per cent graph.

In the example given above, if the 10 per cent temperature was −15° C. this would be plotted against the 40 per cent temperature of −4° C. on Figure 8, and propane and butane values of 1.8 and 29.5 per cent, respectively, obtained. These, however, are not the correct values for the sample, but have been obtained only for purposes of plotting on Figure 11 to obtain the 10 and 40 per cent corrections. When this is done the 10 and 40 per cent corrections of +2.7 and +0.7° C. are respectively obtained. These corrections applied to the above 10 and 40 per cent temperatures give corrected values of −12.3 and −3.3° C., respectively. These corrected values are then plotted on Figure 8 to obtain final correct values of 0.0 and 30.5 per cent for the propane and butane fractions.

It was also found necessary to apply a correction to the 70 per cent temperature in the case of samples high in hexane

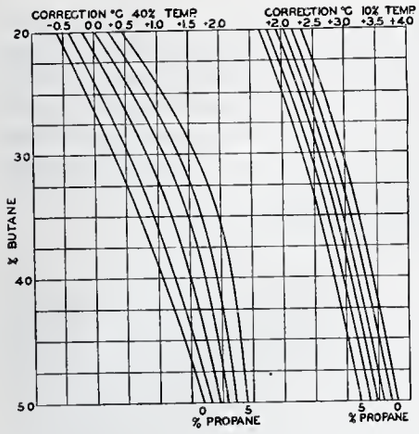

Figure 11. Chart for Correcting 10 and 40 Per Cent Temperatures for Effect of Isomers and Unsaturates in Butane Fraction

plus heavier hydrocarbons, because in such cases this fraction contains much more heptane than the corresponding fraction used in making the synthetic mixtures. One sample of stabilizer bottoms with a content of 42.6 per cent of hexane plus heavier hydrocarbons showed 32 per cent of heptane plus heavier hydrocarbons in this fraction, whereas the hexane plus heavier hydrocarbons used in making the synthetic mixtures had only 11 per cent heptane in the corresponding fraction.

Microfractionation and short-cut runs on several stabilizer bottoms samples established the 70 per cent correction curve shown in Figure 12. It is obvious that since the 70 per cent correction can be correlated with the temperature of the 70 per cent point, Figure 5 could be revised to apply the correction automatically. Such a revision is shown in Figure 13.

With Figure 13 as a basis, the working graph, Figure 14, used in actual analysis of routine samples was prepared by drawing the heavy lines to approximate the positions of the groups of curves on the former figure and dividing the intervening spaces into equal parts. The method of constructing Figure 14 involves the assumption that for a given pentane-hexane ratio, the 40 to 70 per cent points fall on a single curve, if the concentrations of propane and butane are within the range covered by the graphs. This is not strictly true, but was assumed for the sake of simplicity, and does not involve a serious error.

It will be observed that if the 40 to 70 per cent temperature of an unknown sample does not fall on a point corresponding to one of the 10 to 40 per cent curves, it will be necessary to extrapolate between the two curves between which this temperature falls. For this purpose extrapolation data are provided with each 10 to 40 per cent curve which correct the 10 and 40 per cent temperatures, so that the graph is applicable to the sample under consideration. These data were calculated by noting the average difference in temperature between corresponding points on consecutive 10 to 40 per cent graphs, and dividing the difference into five equal portions. As indicated in the extrapolation data, one or two of these portions are added to or subtracted from the experimental 10 to 40 per cent temperatures to make the curve nearest them applicable.

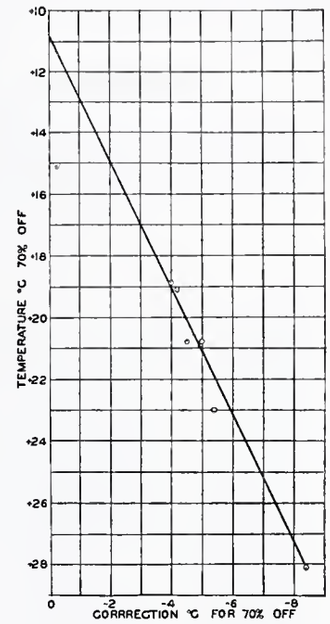

Figure 12. Curve for Correcting 70 Per Cent Temperature for Effect of Heptanes and Heavier in Hexane+ Fraction

For example, if a sample had 40 and 70 per cent temperatures of +1 and +19.7° C., respectively, a pentane-hexane ratio of 0.769 would be obtained from Figure 14, since this line lies nearest the point. There is no 10 to 40 per cent graph corresponding to this value, but the graph nearest this value is Figure 9 with a pentane-hexane ratio of 0.666 and under "Extrapolation Data" with this graph will be found the ratio 0.769 together with 10 and 40 per cent temperature correction values which, when applied to the 10 and 40 per cent temperatures for the sample, make the graph applicable to its analysis. This procedure was adopted to avoid the necessity of making up 10

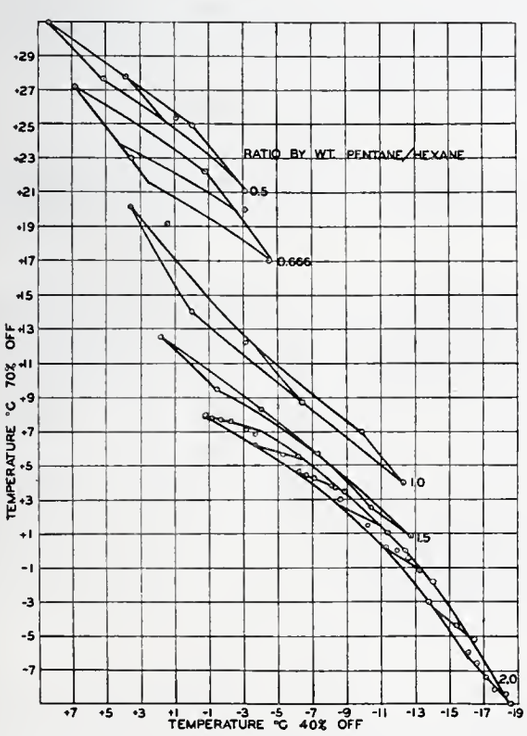

Figure 13. 40 and 70 Per Cent Temperatures after Applying Corrections Indicated in Figure 12

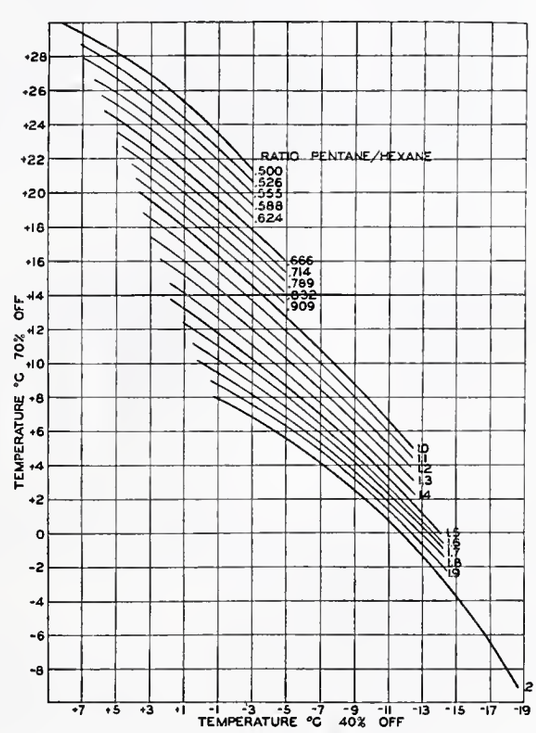

Figure 14. Working Graph for 40 to 70 Per Cent Temperatures, Prepared on Basis of Figure 13

to 40 per cent graphs corresponding to all possible pentane-hexane ratios.

Accuracy of Method

The accuracy of this method is limited by that of the microfractionation column used to analyze the materials required in making up the synthetic mixtures. However the analyses

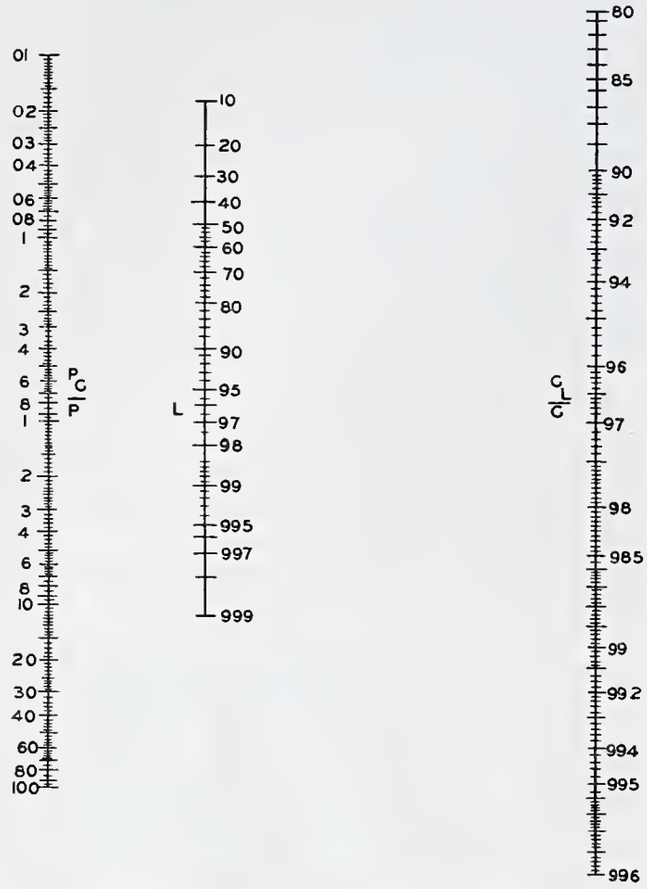

Figure 15. Nomograph for Calculating Liquid-Vapor Equilibria for Small Amounts Vaporized

were carefully carried out by an experienced operator and are believed to be of a high order of accuracy. The short-cut runs, both synthetic and routine, are highly reproducible. A comparison of short-cut and microfractionation analyses on several routine samples is given in Table II.

Table II. Comparative Analyses

Sample	Short-Cut Weight Per Cent				Microfractionation Weight Per Cent			
	Propane	Butane	Pentane	Hexane	Propane	Butane	Pentane	Hexane
1	1.0	25.8	31.8	41.4	0.9	25.4	31.2	42.5
2	0.7	26.3	27.0	46.0	0.9	26.3	26.4	46.4
3	1.4	27.5	29.6	41.5	1.1	27.1	29.5	42.3
4	0.0	26.3	30.6	43.1	0.0	26.6	31.0	42.4
5	3.6	22.0	25.6	48.8	3.2	22.4	24.5	49.9
6	0.0	25.5	28.7	45.8	0.0	25.6	29.2	45.2
7	1.9	44.4	33.6	20.1	1.7	43.6	34.7	20.0

These data show that this method checks the microfractionation column within 0.5 per cent on the propane fraction, 1 per cent on the butane fraction, and 2 per cent on the pentane and hexane fractions.

In the preparation of these graphs, every effort was made to avoid complications whenever possible. It would be possible to reconstruct the graphs in Figures 6, 7, 8, 9, and 10 so that the corrections in Figure 11 would be automatically applied, as was done in the case of Figure 5, but it was felt that the 70 per cent correction would probably be fairly constant for all sorts of samples whereas the 10 and 40 per cent corrections would probably not be constant. The 10 to 40 per cent corrections presented are based on an average boiling point of −3.2° C. for the butane fraction of the stabilizer bottoms. Accordingly, it is desirable to determine the average boiling point of the butane fraction of the stabilizer bottoms to be analyzed and to alter the 10 to 40 per cent correction curves accordingly. It is believed that under ordinary operating conditions the average boiling point of the butane fraction would not change appreciably from day to day.

Advantages of Short-Cut Method

The short-cut method for control purposes offers several advantages over fractional distillation. The time required for a short-cut analysis is about 1.5 hours, including calculations, while a similar analysis by fractionation would take about 3.5 hours for a gas sample and 6 hours for a liquid sample. The operation is simple and does not require as great expertness for good results as microfractionation; furthermore the operation, being largely automatic, is less subject to the human element, which often leads to widely divergent results in microfractionation, especially in routine analysis.

Rosen and Robertson (7) describe the analysis of stabilizer reflux by the short-cut method without the use of liquid nitrogen and it is known that such analysis may be used to calculate the amount of butane in the stabilizer gas. Since the analysis of stabilizer bottoms by the short-cut method does not require liquid air, the short-cut apparatus, using solid carbon dioxide as the cooling agent, permits complete analytical control over the operation of the stabilizer.

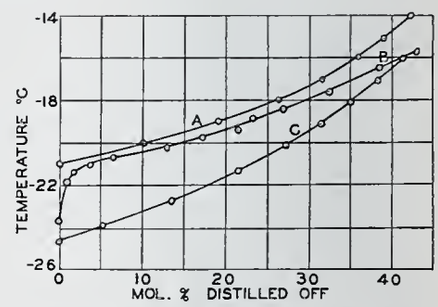

Figure 16. Comparison of Calculated and Synthetic Distillation Curves

A and *C* calculated, *B* synthetic run

Composition	Weight Per Cent *A*	*B*	*C*
Butylene	..	..	26.5
Butane	50	50	23.5
Pentane	33.3	33.3	33.3
Hexane	16.7	..	16.7
Hexane +	..	16.7	..

Acknowledgment

The authors are indebted to J. B. Maxwell, of the Engineering Department of this company, for the preparation of the nomographic chart used in calculating the distillation curves.

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Correction. In the article entitled "Asbestos in Permanganate Titrations" by Curtis and Finkelstein [Ind. Eng. Chem., Anal. Ed., **5**, 318 (1933)] the second line in the second column on page 318 should read "in a typical limestone carrying 54 per cent of calcium as calcium oxide."

New Volumetric Method for Determination of Sulfate

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A direct volumetric method is described. Standard barium chloride solution is added to the solution containing sulfate, using mercuric nitrate as an outside indicator. A technic is described in which a preliminary end point is reached several cubic centimeters in advance of the final end point, enabling the analyst to add the bulk of the barium chloride solution rapidly.

It has long been known that when sulfate solutions are added to mercuric nitrate solutions under the proper conditions a yellow colored, basic mercuric sulfate, known as "turpeth," precipitates (*2*). It occurred to one of the authors that this substance, because of its color, might serve as an indicator in a volumetric sulfate analysis. It could not be used successfully in the titration mixture, but when employed as an outside indicator the results were of such accuracy that the authors believe the method to be of value.

This paper describes the titration, together with experiments designed to determine favorable conditions under which it should be carried out.

Experimental

Preparation of Reagents. Good grades of potassium sulfate and barium chloride dihydrate were further purified by recrystallization, and solutions of the two salts were made in distilled water.

Mercuric nitrate solution was prepared by dissolving mercuric oxide in nitric acid. After some experiments the following preparation was used:

Twenty grams of mercuric oxide were treated with 18 cc. of nitric acid, made by diluting 10 cc. of strong acid (specific gravity, 1.42) with water. The mixture was stirred with a glass rod, and the reaction allowed to take place until the solution became strongly turbid. It was then filtered, and to the filtrate were added 6 cc. of water. The solution was allowed to stand several hours before using. During this time a light-colored, crystalline precipitate of basic mercuric nitrate separated out. For best results it was found essential to have the acidity of this indicator solution as low as possible, and to insure this the presence of the basic nitrate precipitate was required.

A color standard was used in determining the end point, and after a number of experiments the following simple preparation was employed:

Potassium sulfate (4.3 grams) and 0.2 gram of potassium dichromate were dissolved in a liter of water. Eight grams of barium chloride dihydrate were dissolved in another liter of water. To make up the color standard 10 cc. of the sulfate-dichromate solution were pipetted into a small flask, and 10 cc. of the barium chloride solution were added with swirling. Fresh standard was made up each day from the stock solutions.

All flasks, pipets, and burets used in the work were calibrated at least twice.

Technic Used in Titration. Barium chloride solution (0.02 to 0.07 *M*) was added to potassium sulfate solution (0.005 to 0.02 *M*) from a buret, both solutions being at room temperature. The initial volume of the sulfate solution was in most cases 100 cc. In the titration flask a medicine dropper with an extra-long glass tube (22 cm.) was used for obtaining test portions. The titration mixture was vigorously swirled before taking out test portions. The barium chloride solution was added slowly (about 15 cc. per minute), and in the case of very dilute solutions the titration mixture was allowed to stand after each addition for at least a minute (Table II) before taking out test portions.

A drop of mercuric nitrate solution was put in each of the outer depressions of a clean spot plate with another dropper. In each of the two inside depressions were put 4 drops of well-mixed color standard from a third dropper. The color tests were made by allowing a drop of the titration mixture to fall into a drop of the mercuric nitrate solution on the spot plate. The time was then noted, by counting slowly, or with a watch, when the color of the mixture just exceeded that of the standard in intensity. When the tests were made in this manner the color exceeded that of the standard almost immediately up to within a few cubic centimeters of the end point. At this stage the amount of titration mixture was increased to 3 or more drops per test. Upon the addition of more barium chloride solution the time interval before the appearance of the proper yellow color rapidly increased, as shown in Figure 1. An interval of 30 seconds was chosen as the end point. The buret volume corresponding to this time was calculated by interpolation between the two time intervals on either side of the 30-second point, although a fair degree of accuracy could be obtained by calling that reading closest to 30 seconds the end point.

Spot plates were cleaned with cleaning solution and water, dried with filter paper, and then rinsed with ether. It was found helpful to remove all grease, so that the drops of liquid flattened out properly. Experiments were carried out using a spherically shaped drop, such as described by Pond (*1*) for the zinc ferrocyanide titration, but satisfactory results could not be obtained in the present determination.

A daylight-type electric lamp was used in the work. In determining the time intervals, a greater accuracy resulted if the spot plate was moved around so that the test mixture was always on the same side of the standard.

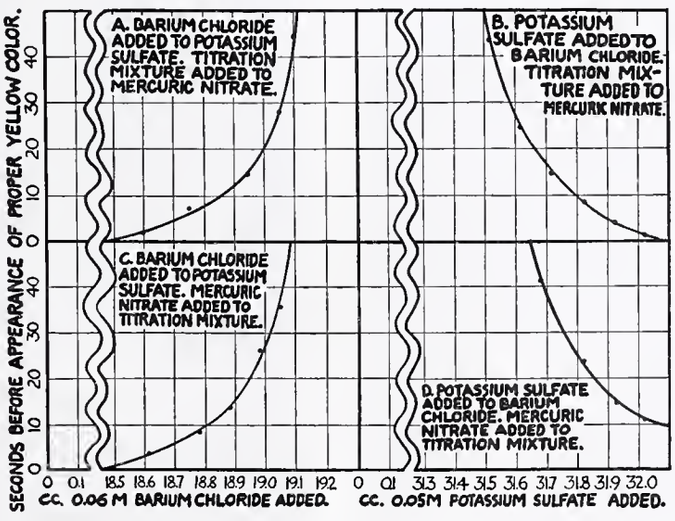

Figure 1. Effect of Order of Addition of Reagents

Order of Addition of Reagents. Four experimental procedures were tried in determining the best order of addition of reagents. Barium chloride solution was added to potassium sulfate solution, and vice versa, and on the spot plate the titration mixture was added to mercuric nitrate solution, and the reverse. An experimental curve for each of these titrations is given in Figure 1.

Table I. Effect of Order of Addition of Reagents upon Sensitivity

Order of Addition	Sensitivity (Mean of several)
1. 0.0501 *M* potassium sulfate solution added to 100 cc. of 0.0155 *M* barium chloride solution. Mercuric nitrate solution added to titration mixture on spot plate	90
2. 0.0501 *M* potassium sulfate solution added to 100 cc. of 0.0155 *M* barium chloride solution. Titration mixture added to mercuric nitrate solution on spot plate	140
3. 0.0621 *M* barium chloride solution added to 100 cc. of 0.0125 *M* potassium sulfate solution. Titration mixture added to mercuric nitrate solution on spot plate	200
4. 0.0621 *M* barium chloride solution added to 100 cc. of 0.0125 *M* potassium sulfate solution. Mercuric nitrate solution added to titration mixture on spot plate	150

The sensitivity at the end point will be defined as the reciprocal of the number of milliequivalents of reagent being added from the buret necessary to cause the time interval (before the appearance of the proper yellow color) to change from 25 to 35, or from 35 to 25 seconds. Thus the larger the sensitivity the sharper the end point. The sensitivity for each of these procedures is given in Table I.

The average deviation from the mean for these sensitivities is about ±30. It was decided from the results in Table I that procedure 3 was the best, and this was used for all later work.

Strength of Indicator. Many concentrations of mercuric nitrate were tried. Among the higher concentrations very little difference in behavior was observed, but with dilute solutions a definite drop in sensitivity was apparent. Sensitivities obtained with three concentrations were as follows: 6 *M*, 210; 3 *M*, 220; 0.2 *M*, 130. Approximately 3 *M* mercuric nitrate solution was used for most of the later work.

Reaction Time. The authors were uncertain as to the length of time necessary for the completion of the barium sulfate reaction at room temperature, since it is generally believed that precipitation takes place slowly, even in hot solution. The point was cleared up by mixing various quantities of barium chloride and potassium sulfate solutions, and then noting whether the time interval before the appearance of the proper yellow color (in test portions) changed with time. The results are given in Table II.

Table II. Effect of Concentration upon Reaction Time

0.0152 *M* K_2SO_4 23.33 cc. $BaCl_2$		0.0050 *M* K_2SO_4 7.63 cc. $BaCl_2$		0.0025 *M* K_2SO_4 3.70 cc. $BaCl_2$	
Seconds for yellow color to appear	Minutes after adding $BaCl_2$	Seconds for yellow color to appear	Minutes after adding $BaCl_2$	Seconds for yellow color to appear	Minutes after adding $BaCl_2$
33	1.5	4	0.5	0	1
37	3	9	1	3	1.5
37	6	27	2	12	2
34	14	27	3	18	3.5
40	15	26	5	32	5
35	21	..	..	27	7
..	..	..	..	25	12
..	..	..	..	30	23

100-cc. samples of potassium sulfate solution used. 0.0621 *M* barium chloride solution added. Titration carried out in neutral solution.

Even when using as dilute a potassium sulfate solution as 0.0025 *M* the reaction is essentially complete in about 5 minutes. Titration at room temperature therefore appears to be entirely feasible. However, it is probable that certain types of impurities cause a slower reaction rate than this.

Relation of End Point to Stoichiometrical Point. The 30-second end point and the stoichiometrical point do not coincide under the (otherwise) most favorable conditions so far worked out. Thus when 0.0621 *M* barium chloride solution was added to 100 cc. of 0.0125 *M* potassium sulfate solution (neutral), 19.16 cc. were required, while the stoichiometrical amount necessary was 20.13 cc.

The error may of course be overcome by standardizing the barium chloride solution with an easily purified sulfate, such as potassium sulfate. This procedure should be followed in any event, since both barium chloride dihydrate and anhydrous barium chloride are poor standards.

Effect of Acidity. The acidity of the titration mixture was found to affect markedly the position, sensitivity, and reproducibility of the end point. Results of experiments on this phase of the work are given in Table III. A neutral or slightly acid solution appears to be the best in running the titration. Experiments carried out at higher acidities and alkalinities than those of Table III gave, in general, more erratic results and lower sensitivities.

Table III. Effect of Acidity

Solution Being Titrated			0.0621 *M* $BaCl_2$ Required from Buret[a]	Mean Sensitivity
0.0501 *M* K_2SO_4	Water	0.1 *N* Acid or base		
Cc.	*Cc.*			
25.00	73	2 cc. NaOH	20.02 ± 0.04	170
25.00	75	None	19.16 ± 0.01	200
25.00	73	2 cc. HCl	18.91 ± 0.01	190
25.00	70	5 cc. HCl	18.86 ± 0.01	200
25.00	65	10 cc. HCl	18.74 ± 0.05	130

[a] Average of four determinations in each case.

Effects of Other Ions. Titrations of potassium sulfate solutions were carried out in the presence of five times the amount (equivalents) of other salts, in neutral solution. The results are given in Table IV. The errors are seen to be smallest, on the whole, when the solutions were most dilute. Nitrates caused large errors in dilute solution, although in more concentrated solution the error due to calcium nitrate was smaller and different in sign. The results can be explained, for the most part, by assuming precipitation of complexes of the type (Ba, K)SO_4 when the results were low, and Ba(SO_4, NO_3) when the results were high.

Table IV. Effect of Impurities

Molality[a] of $BaCl_2$ Solution	$BaCl_2$ Solution	Impurity	Nature of Impurity	SO_4 Present	SO_4 Found	Error
	Cc.	*Grams*		*Gram*	*Gram*	*Gram*
0.0219	22.9	None	None	0.0482	0.0482	....
0.0219	22.7	0.24	$MgCl_2$	0.0482	0.0478	−0.0004
0.0219	22.9	0.24	$MgCl_2$	0.0482	0.0482	0.0000
0.0219	22.8	0.24	$MgCl_2$	0.0482	0.0480	−0.0002
0.0219	22.6	0.29	NaCl	0.0482	0.0476	−0.0006
0.0219	22.6	0.29	NaCl	0.0482	0.0476	−0.0006
0.0219	22.9	0.41	$NaC_2H_3O_2$	0.0482	0.0482	0.0000
0.0219	22.6	0.41	$NaC_2H_3O_2$	0.0482	0.0476	−0.0006
0.0219	22.7	0.83	KI	0.0482	0.0478	−0.0004
0.0219	22.6	0.83	KI	0.0482	0.0476	−0.0006
0.0219	22.4	0.21	LiCl	0.0482	0.0471	−0.0011
0.0219	22.6	0.21	LiCl	0.0482	0.0476	−0.0006
0.0600	20.86	None	None	0.1202	0.1202	....
0.0600	20.30	0.73	NaCl	0.1202	0.1170	−0.0032
0.0600	20.24	0.73	NaCl	0.1202	0.1166	−0.0036
0.0653	19.16	None	None	0.1202	0.1202	....
0.0653	18.70	0.51	LiCl	0.1202	0.1173	−0.0029
0.0653	18.63	0.51	LiCl	0.1202	0.1169	−0.0033
0.0653	18.64	0.51	LiCl	0.1202	0.1169	−0.0033
0.0653	18.73	0.51	LiCl	0.1202	0.1175	−0.0027
0.0653	18.97	1.03	$Ca(NO_3)_2$	0.1202	0.1190	−0.0012
0.0653	18.87	1.03	$Ca(NO_3)_2$	0.1202	0.1184	−0.0018
0.0653	18.83	1.03	$Ca(NO_3)_2$	0.1202	0.1181	−0.0021
0.0653	18.85	1.03	$Ca(NO_3)_2$	0.1202	0.1182	−0.0020
0.0219	22.9	None	None	0.0482	0.0482	....
0.0219	23.3	0.41	$Ca(NO_3)_2$	0.0482	0.0490	+0.0008
0.0219	23.7	0.41	$Ca(NO_3)_2$	0.0482	0.0499	+0.0017
0.0219	24.5	0.43	$NaNO_3$	0.0482	0.0516	+0.0034
0.0219	24.0	0.43	$NaNO_3$	0.0482	0.0505	+0.0023
0.0219	26.6[b]	0.36	$Al(NO_3)_3$	0.0482	0.0560	+0.0078

[a] Solutions standardized against potassium sulfate.
[b] Solution acid.

It is to be noted that while some of the errors involved are rather serious, they can be largely corrected by having an approximately equal amount of the impurities in the sulfate solution used to standardize the barium chloride.

Interfering Substances. The titration cannot be carried out in the presence of appreciable amounts of ammonium

compounds, as they prevent the formation of basic mercuric sulfate. The titration is also unsuccessful in the presence of ions that cause precipitates with mercuric nitrate, or with barium chloride, such as tartrates, phosphates, etc. Potassium iodide is an exception (Table IV). The insoluble mercuric iodide could be made to dissolve in excess mercuric nitrate solution by stirring the color test mixture with a glass rod, and the end point could then be determined as usual. Colored substances may also make the end point difficult or impossible to detect.

Table V. Effect of Solid Barium Sulfate upon End Point

Titration Mixture per Drop $Hg(NO_3)_2$	0.0207 *M* $BaCl_2$ Solution Needed per Millimol $BaSO_4$ 100 cc. Neutral K_2SO_4 Solution		
	About 0.12 g. $BaSO_4$ formed	About 0.24 g. $BaSO_4$ formed	About 0.36 g. $BaSO_4$ formed
Drops	*Cc.*	*Cc.*	*Cc.*
2	42.2	44.0	44.3
3	44.7	45.2	45.3
4	45.5	45.8	45.7
5	46.0	46.2	45.9

Effect of Barium Sulfate Concentration on End Point. The effect of concentration of barium sulfate, and of the number of drops of titration mixture per drop of mercuric nitrate on the position of the end point was determined in neutral solution, using 0.02 *M* barium chloride solution. The results, given in Table V, indicate that the error due to difference in concentration of barium sulfate may be minimized by taking a sufficient number of drops of titration mixture near the end point. This is also recommended because the end point is then more sensitive and closer to the stoichiometric point. A small-sized drop of mercuric nitrate is also advantageous, since the same effect can then be produced with a smaller amount of titration mixture.

Discussion

The method is recommended for routine analysis, rather than for single determinations. All the solutions involved are of stable inorganic compounds, and can be made up in large quantities and kept for long periods of time.

The biggest advantage of the method is that it is time-saving. The authors are able to finish an ordinary titration, working individually and not knowing the sulfate content, in about 10 minutes. This is possible, in spite of the outside indicator, because the method is a direct one, and because a preliminary end point is reached (using one drop of titration mixture) several cubic centimeters in advance of the final end point (using several drops of titration mixture). Thus the barium chloride solution can be added 2 or 3 cc. at a time until the final end point is nearly reached. The apparatus necessary is also simple and inexpensive.

No attempt will be made here to give further procedure for the method other than that connected with the titration itself, because of the great variety of substances and solutions in which sulfate may be determined.

Aside from any analytical considerations, the method employed in obtaining Table II seems to be useful in measuring the rate of formation of barium sulfate under various conditions.

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Chemical Examination of Trichloroethylene for Anesthesia

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Among the various chemical compounds recently used for local anesthesia is trichloroethylene, $CHCl{=}CCl_2$. This compound has been described in the literature since 1864; it is not, therefore, a new substance. During the World War, Plessner (*2*) found symptoms of poisoning in men using trichloroethylene for removing grease from metal parts of machinery, and noted that the poison had special affinity for the sensory fibers of the trigeminal nerve. Oppenheim (*1*) recognized the possibility of lessening sensitiveness of the diseased trigeminal nerve in cases of facial neuralgia by giving the patient small doses of this compound to inhale.

Trichloroethylene has also been developed commercially as a low-boiling, noninflammable solvent for extracting oils, fats, and waxes, for degreasing metals, and for purposes of dry cleaning. For these uses, a rather impure "factory" grade ordinarily has been sufficient. For therapeutic purposes, only a much more refined product is suitable.

Several firms have been supplying medicinal trichloroethylene under various brand names, such as Westrosol, Gemalgene, Chlorylen, and Trethylene. Trichloroethylene was presented to the Council on Pharmacy and Chemistry of the American Medical Association for inclusion in "New and Nonofficial Remedies" and the Chemical Laboratory was asked to make an examination of the product. Accordingly, examination was made of two brands of trichloroethylene preparations presented; a specimen of Eastman grade and of a practical grade purchased from Eastman Kodak Co.; and another brand used medicinally, obtained on the open market. The results of this investigation are given in Table I, which includes qualitative and quantitative determinations.

The boiling point range of Chlorylen and of Trichloroaethylen zu Chlorylen was determined after extraction of the preparation with an equal volume of water to remove any interfering substances such as alcohol, and subsequent drying of the trichloroethylene layer with anhydrous sodium sulfate. After being notified of the results of the investigation of Chlorylen, the firm indicated a desire to investigate further, and to submit the product again in the future.

Based in part on the information in the literature and on the results of the work reported herein, somewhat rigorous standards for identity and purity were elaborated. These were sent for comment to the firm which submitted the product; then in due time the following standards were adopted by the Council on Pharmacy and Chemistry for inclusion in "New and Nonofficial Remedies."

Standards

Trichloroethylene.[1] Trichloroethylenum, trichlorethylene, $CHCl{:}CCl_2$, 1-chloro-2-dichloroethylene.

[1] Solutions referred to in the descriptions of qualitative and quantitative tests are, unless otherwise stated, of the strength described in the current U. S. Pharmacopeia.

Table I. Examination of Trichloroethylene and Trichloroethylene Preparations

	Beilstein I, 4th ed.	N. N. R. Standards	Calco Bulk Sample	Calco Ampules	Trethylene[a]	Eastman	Eastman (Practical)	Trichloroethylen[b] zu Chlorylen	Chlorylen[b] (Market Specimen)
Boiling point range (U. S. P. X method, 760 mm.)	87.15	86–88	86.1–88.0	85.4–87.4	83.8–88.0	85.4–87.9	85.6–88.2	85.7–88.2	85.7–89.6
Specific gravity, 25° C./25° C.	1.4598 (25.5/25.5)	1.458–1.460	1.460	1.460	1.452	1.460	1.460	1.450	1.447
Refractive index, 20° C.									
a. Original	1.4777 ($n_D^{19.8}$)	1.4770–1.4780	1.4777	1.4775	.....	1.4770	1.4774	1.4767	1.4755
b. Distillate	.....	1.4770–1.4780	1.4770	1.4776	.....	1.4774	1.4774	1.4774	1.4774
Titration of aqueous extract, 0.01 *N* HCl or NaOH consumed	.....	Not more than 0.1 cc. 0.1 *N*	0.05 cc.	1.05 cc.	0.40 cc.	Negligible	Negligible	Less than 0.1 cc. 0.1 *N*	Less than 0.1 cc. 0.1 *N*
Residue on evaporation, 100° C.	.....	Not weighable (25 cc.)	Less than 0.0001 gram	.....	Less than 0.0001 gram	0.0001 gram	0.0002 gram	.....	0.0004 gram
QUALITATIVE TESTS									
Bromine test (lower layer)	.....	White turbidity	White turbidity	.....	.....	White turbidity	White turbidity	.....	White turbidity
Silver ammonium nitrate (turbidity in 10 min.)	.....	None	None	Slight	Slight	Darkened aqueous layer	Blackened aqueous layer (much less for distillate)	..... Turbid	Immediate turbidity
Chlorides (turbidity in 5 min.)	.....	None	None	Practically none	Practically none	Practically none	Practically none	None	None
Readily oxidizing substances (chlorine, etc., blue color)	.....	None	None	None	None	None	None	None	None
Turbidity test (alcohol)	.....	Turbid	Turbid	.....	.....	Turbid	Turbid	.....	Turbid

[a] Davies, Rose & Co [b] Schering Corp.

Actions and Uses. The actions of trichloroethylene have not been investigated comprehensively, and it was introduced into therapeutics following some observations on man. Trichloroethylene appears to have a selective action on the sensory endings of the trigeminal nerve, whereby it affords relief in trigeminal neuralgia, but it is not clear that the action even of therapeutic doses is limited to these endings, and different individuals seem to show rather wide differences in susceptibility to this action; hence the dose necessary to afford relief varies correspondingly. Therapeutic doses sometimes cause transitory giddiness, with lassitude, distress, palpitation, and nausea. Large doses cause narcosis, and excessive doses cause death. There was no perceptible injury to the lungs, heart, or liver after narcosis repeated several times in the dog, but there was slight hyperemia of the gastric mucous membrane and marked reddening of the duodenum. The liquid is irritant; hence it should not be allowed to come in contact with the nose when the vapor is inhaled.

Dosage. Fifteen minims by inhalation, to be repeated after a few minutes if necessary; but it appears probable that not more than 60 minims should be inhaled within 24 hours when it is used for any considerable period of time.

Trichloroethylene occurs as a clear, colorless, mobile, and volatile liquid, possessing an odor similar to that of chloroform. It is miscible with ether and very soluble in alcohol; it is practically insoluble in water. The specific gravity is from 1.458 to 1.460 at 25° C. The refractive index is from 1.4770 to 1.4780 at 20° C.

Transfer 25 cc. of trichloroethylene to a distilling flask. Determine the distillation range according to Method I of U. S. Pharmacopeia X. Ninety-five per cent distills over at from 86° to 88° C. (corrected) at 760 mm. The refractive index of the distillate is the same as that of the material before distillation.

Transfer 5 cc. of trichloroethylene to a glass-stoppered cylinder, add 5 cc. of bromine water and shake the mixture vigorously at intervals of 15 minutes: at the end of an hour a white turbid solution forms in the lower layer. Agitate gently 5 cc. of trichloroethylene with 2 cc. of silver ammonium nitrate solution in a narrow glass-stoppered cylinder of from 10 to 15 cc. capacity: No turbidity or darkening is observed in either layer at the end of 10 minutes (acetylene, etc.).

Agitate 20 cc. of trichloroethylene with a 50-cc. portion of water and repeat, using a 25-cc. portion of water; transfer the combined aqueous layer to a flask and add to the aqueous solution 2 drops of methyl red indicator solution. If the color of the solution is yellow, not more than 0.1 cc. of 0.1 *N* hydrochloric acid is required to assume a pink color; if the color of the solution is pink, not more than 0.1 cc. of 0.1 *N* sodium hydroxide is required to assume a yellow color.

Agitate 10 cc. of trichloroethylene with 25 cc. of water and allow the liquid to separate completely. Separate 10-cc. portions of the aqueous layer are affected as follows: No turbidity is noted 5 minutes after the addition of 0.1 cc. of nitric acid and 0.1 cc. of silver nitrate solution (chlorides); no blue color is observed after the addition of 0.1 cc. of potassium iodide test solution and 0.1 cc. of starch test solution (readily oxidizing substances such as free chlorine).

Add 0.1 cc. of alcohol to 5 cc. of trichloroethylene: A turbid solution is formed (distinction from chloroform).

Evaporate 25 cc. of trichloroethylene in a platinum or porcelain dish on a steam bath and dry to constant weight at 100° C. No weighable residue is obtained.

Summary

Comparative chemical examinations were made of several brands of medicinal trichloroethylene and of a specimen of a purified and of a technical grade. Two products were found to be markedly outside of the boiling point range and specific gravity range. The acidity of all samples but one examined was well within the range set. Four samples showed considerable turbidity in both layers when the silver ammonium nitrate test was applied. The presence of this turbidity gives rise to considerable doubt as to whether compounds such as acetylene are absent. All samples indicated a lack of chlorides and of readily oxidizing substances.

Standards for trichloroethylene for medicinal uses have been prepared, based upon the literature and upon the work herein reported.

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Correction. In the article on "Estimation of Total and Bound (D) Gossypol in Cottonseed Meal" by Smith and Halverson [Ind. Eng. Chem., Anal. Ed., 5, 319 (1933)], 13th line from the bottom of the second column on the page, the sentence should read "Pipet (by suction) 4 cc. of aniline onto the meal."

Optical Density Color Measurement for Petroleum Oils

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METHODS used in this country for assigning numerical color values to petroleum lubricating oils may be grouped as follows:

Class 1. A given thickness of oil is matched against one of a set of glass or liquid standards, primarily on the basis of hue. In this class fall the Lovibond (*7*) and the National Petroleum Association (*1*) scales.

Class 2. A variable thickness of oil is matched against a standard color disk, as in the method initially described by Delbridge (*5*) and later applied in the Tag-Robinson[1] colorimeter (*13*); or against a fixed depth of liquid standard, as in the methods of Rogers, Grimm, and Lemmon (*10*) and of Weir, Houghton, and Majewski (*12*). In at least one of these (*12*) the match is made on the basis of equality of brightness. A variant of methods of this class consists in matching a fixed thickness of the oil sample against a variable thickness of oil standard, as in the method of Parsons and Wilson (*9*). The color values derived from the methods of class 2, with the exception of the Tag-Robinson colorimeter, have been called "true colors."

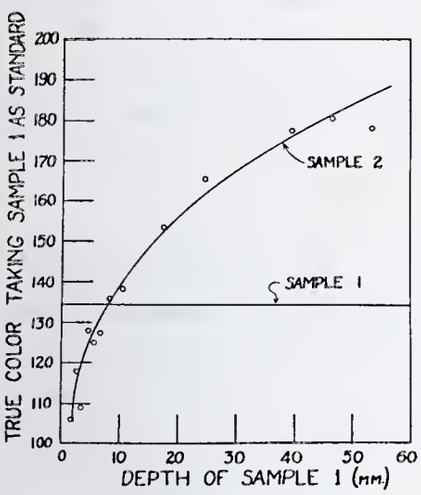

Figure 1. Reversal in Apparent True Color with Different Depths of Oils

Class 3. The fraction of light absorbed by a certain thickness of oil is determined photometrically. Examples of this class are the instrument proposed by Cox (*3*) which uses a sectored flicker disk, and that of Story and Kalichevsky (*11*) in which the distance between sample and illuminant is varied and the inverse-square law employed. Apparatus in which the relative transmission of unknown and standard oils are indicated by the response of photoelectric cells have been developed by several of the instrument companies. In all the methods cited except one (*3*) white light has been used as illuminant.

While several of these methods have been useful in the specification of color for sales work, from the viewpoint of the refiner each has more or less serious shortcomings. In order to serve him best, a color scale must meet six specifications:

1. Samples should be accorded values in agreement with ordinary visual inspection.
2. Values should be additive in the sense that the color C_m, of a mixture of two oils having colors C_a and C_b, will be given by the equation

$$C_m = \frac{C_aV_a + C_bV_b}{100} \qquad (1)$$

where V_a and V_b are the respective percentages (by volume) of the oils whose colors are C_a and C_b.
3. Apparatus, standards, and color values should be reproducible in any laboratory.
4. Color values should be based on fundamental rather than arbitrary units.
5. The method should be usable in routine work.
6. Consistent color values should be obtainable on oils ranging from light finished products to the darkest tars and bottoms.

[1] The Saybolt chromometer for measuring the color of gaolines and naphthas falls in this class.

The methods of class 1 fail to meet specification 2. (For example, a mixture of equal parts of two finished oils from the same stock, which have respective N. P. A. colors of 4 and 8, may have an N. P. A. color of 6.5, whereas Equation 1 would require an N. P. A. color of 6 for the mixture. Story and Kalichevsky (*11*) show that the Lovibond scale leads to oil colors which are far from additive in the sense of Equation 1.) The methods of class 2 when restricted to matching a variable thickness of oil against a fixed thickness of one standard, as prescribed in the most recently published example (*12*) of the class, yield color values which satisfy specifications 1, 2, and 6, but do not meet specifications 3 and 4, and could be better with regard to specification 5. The methods of class 3 fail to meet either specification 1 (*3*) or specification 2 (*11*). (The method of Cox is open to objection because of his choice of blue light as illuminant, rather than because of his photometric arrangement.) When photocells are used with white light as illuminant it is well to remember that the response curve of the cell may vary markedly from that of the normal eye (the so-called visibility curve). O'Brien (*8*) has shown that filters can be devised for at least one type of photocell, such that the response curve of the combination is in satisfactory agreement with that of the eye.

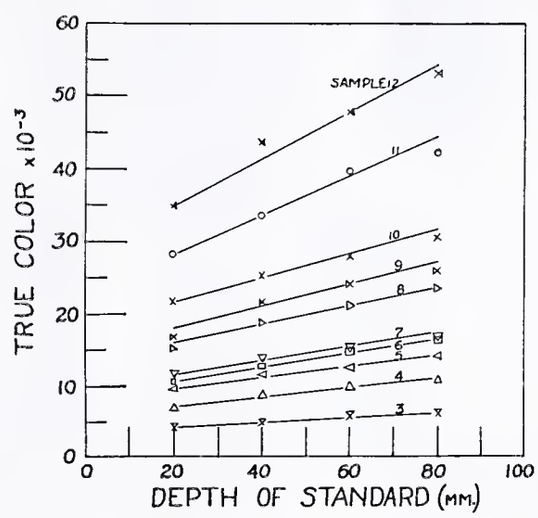

Figure 2. Variation of Apparent True Color of Dark Oils* Matched against Various Depths of Standard

* 0.1 to 2.0 per cent solution in ethylene dichloride.

This paper presents experimental data to show how a color scale for petroleum lubricating oils was developed, which meets all six of the above specifications. A complete description of the final method is also given, with examples of determinations on a large number of oils.

Experimental

One of the most serious objections to the true color method of determining oil colors is the change in apparent true color with the nature of the standard oil (*10*) or with the depth of standard against which the match is made. Figure 1 shows the results of an experiment in which two oils of nearly the same N. P. A. colors were compared in the Duboscq colorimeter, using white light. (These and subsequent

samples are described in Table I). Sample 1 is taken as standard and is therefore assigned the same true color at all depths. It is obvious that sample 2 will be assigned a true color less than, equal to, or greater than sample 1, if the depths matched are varied from lesser to greater. Furthermore these effects become greater when the difference of type between sample and standard increase. This is exemplified in Figure 2, which shows the results of matching ethylene dichloride solutions of various dark oils against a 2.5 + N. P. A. oil standard. Another difficulty with the true color method lies in the choice of a proper diluent for dark oils. Figure 3 illustrates the spread in true color values which may be introduced by the use of a poor solvent such as kerosene. It is evident that for this particular oil benzene is a superior diluent.

Table I. Description of Samples

Sample	Type	Oils Used in Tests: ° A. P. I.	Viscosity S. U. Seconds At 100° F.	At 210° F.
1	7 N. P. A. oil standard	..	...	...
2	7.25 N. P. A. clayed distillate	..	...	...
3[a]	Distillate	20.4	...	160
4[a]	Crude residuum	18.0	...	270
5[a]	Crude residuum	17.1	...	231
6[a]	Crude residuum	14.8	...	401
7[a]	Cracked tar	10.8	196	...
8[a]	Crude residuum	20.6	...	310
9[a]	Crude residuum	17.2	...	252
10[a]	Crude residuum	13.3	...	2141
11[a]	Crude residuum	14.2	...	632
12[a]	Crude residuum	22.8	...	279
13[a]	Finished oil	21.5	...	170
14[a]	Finished oil	21.5	...	170
15[a]	Finished oil	19.4	...	159
16[a]	Distillate	20.9	...	123
17[a]	Crude residuum	8.2	...	1816
18	Finished oil	26.0	145	...
19[a]	Finished oil	22.0	505	...
20[a]	Finished oil	25.0	294	...
21[a]	Finished oil	24.6	278	...
22[a]	Finished oil	28.4	503	...
23[a]	Distillate	20.6	612	...
24	Distillate	24.2	305	...
25	Finished oil	24.6	906	79
26	Finished oil	20.4	590	...
27	Finished oil	23.8	360	...
28	Finished oil	22.0	505	...

Sample	Solutions Used in Tests[b]: Oil	Volume oil × 100 / Volume solution	Diluent
29	Sample 15	2.50	Benzene
30	Sample 16	1.56	Benzene
31	Sample 17	0.10	Benzene
32	Sample 19	6.25	Benzene
33	Sample 4	<1.0	Benzene
34	Sample 9	<1.0	Benzene
35	Sample 10	<1.0	Benzene
36	Sample 20	12.5	Benzene
37	Sample 21	6.25	Benzene
38	Sample 22	6.25	Benzene
39	Sample 23	3.33	Benzene
40	Sample 15	5.00	Benzene
41	Sample 26	50.0	Benzene
42	Sample 10	<1.0	Benzene

[a] Used only in solution.
[b] Excluding those made in true color determinations and accounted for in calculation of true color.

Effects such as these led to a preliminary comparison of several possible diluents—carbon tetrachloride, a narrow-boiling petroleum naphtha, kerosene, medicinal white oil, ethylene dichloride, and benzene. Of these the first three apparently gave incomplete solution, with considerable variation in true color at various dilutions. Medicinal white oil formed more satisfactory solutions but was too viscous for routine use. Ethylene dichloride and benzene were almost equally satisfactory and the latter was chosen for further tests. True color determinations (with fixed depth of standard, *12*) were made on 31 samples each at several dilutions in benzene. Of the 155 determinations so made, 140 gave deviations of less than 5 per cent, 12 of from 5 to 10 per cent, and 3 of from 10 to 15 per cent, from exact proportionality between color and concentration. Figure 4 shows a few of the results. It was concluded that benzene is a highly satisfactory diluent for this purpose.

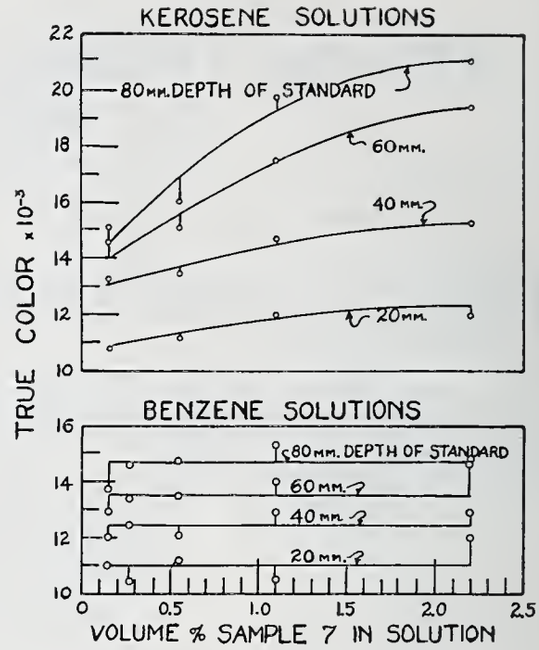

Figure 3. Effect of Diluent on Apparent True Color

In order to eliminate the effect of varying the depth of standard, a study was made of the use of more nearly monochromatic light for illuminating the standard and sample. Three samples were chosen of widely different type, and their true colors were determined both in white light and in the light passed by each of eleven spectral filters by matching against 20 mm. of an oil standard having an N. P. A. color of 2.5+ and assigned a true color of 10 (*12*). (True color values referred to below, unless otherwise stated, will be understood to have been determined by this method. The necessity of defining so precisely the basis of the true color scale, on which these values are reported, emphasizes a major difficulty of the true color method in general—namely, that each investigator has been forced to choose an oil or glass, neither being reproducible, and assign thereto some arbitrary value of true color.) The results, plotted in Figure 5, showed that matching in green light (about 500 to 560 mμ) gave values similar to those obtained in white light. Red light

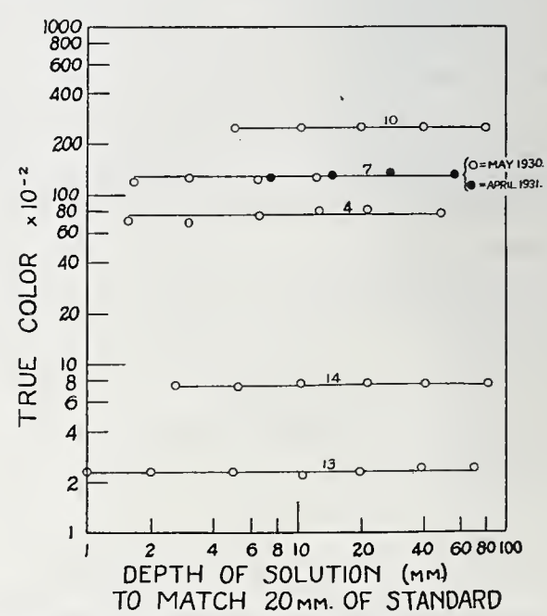

Figure 4. Constancy of True Color over Wide Range of Dilutions

Benzene used as diluent.

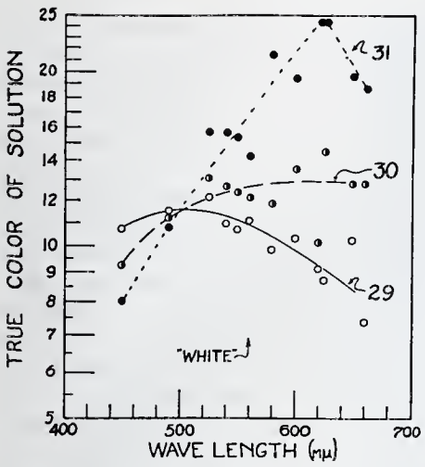

FIGURE 5. EFFECT OF COLOR OF ILLUMINANT ON APPARENT TRUE COLOR

produced too great a spread in the color values, whereas the use of blue light resulted in actual reversals of color. Since each of the points on Figure 5 represents the mean of six readings, it is possible to compare the precision of reading in the several portions of the spectrum by calculating average per cent deviations for each set of six readings. The figures so obtained indicate that the precision of reading is adequate in either blue or green (2 per cent or less average deviation), but decreases considerably in the red (as high as 12 per cent average deviation).

To verify the indication (Figure 5) that green light results in color values concordant with visual comparisons (white light), true color determinations were made on 15 samples in both white and green light. As a matter of interest determinations were also made in red and in blue light. The results, plotted in Figure 6, show a very satisfactory line-up between white and green light. Reversals of apparent color values appear in both the blue and the red (Table II).

Since in monochromatic light the only function of the standard is to absorb a fraction of the incident light, the oil standard was replaced by a neutral filter (gelatin-in-glass) which reduced the intensity to roughly the same extent as 20 mm. of the 2.5+ N. P. A. standard previously used. A coöperative test was then made in which each of two laboratories determined the colors of 79 samples. One laboratory used white light and 20 mm. of oil standard, the other green light and neutral filter standard. The results obtained by the two methods checked satisfactorily, with no trend toward a greater disagreement at either extreme of the color range covered (from 20 to 5100 true color). Since this range of colors required dilutions with benzene such that the resulting solutions contained from 10 to 0.05 per cent of oil, the agreement between the two laboratories also demonstrates that the dilution law holds as well in green light as in white light. Therefore no extensive program to prove this was considered necessary. However, for one case studied, the dilution law held satisfactorily, not only in green light, but also in red and blue. Thus the additivity relations between an oil with color and the proper colorless diluent, such as benzene, follow Equation 1 satisfactorily in green light and would probably do the same in any nearly monochromatic light.

In order to prove that Equation 1 is also satisfied by mixtures containing more than one oil, true colors were determined on four oils of widely different types, and on four two-component blends made from them. The calculated color of the blends agreed with that actually determined within 8 per cent, whether white light and oil standard, or green light and neutral filter standard, were used.

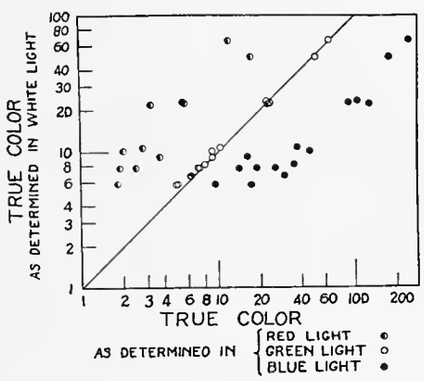

FIGURE 6. RELATION BETWEEN TRUE COLOR IN WHITE LIGHT AND IN RED, GREEN, OR BLUE LIGHT

TABLE II. REVERSALS OF APPARENT COLOR VALUES

Sample	True Color: White light	Green light	Red light	Blue light	N. P. A. Color
27	65.4	65.5	12.2	254	5 −
25	49.9	52.2	17.6	180	4.75+
24	23.4	23.0	5.53	107	3.5+
26	22.9	24.2	5.85	90.3	3.75 −
40	22.5	23.7	3.33	130	3.5+
41	10.8	10.7	2.81	38.5	2.5+
18	10.1	9.32	2.04	47.2	2.5+
34	9.21	9.12	3.80	16.6	1.75
38	8.06	8.10	...	36.4	2.25 −
33	7.63	7.15	2.51	14.5	1.5 −
37	7.60	7.40	...	26.3	2.25 −
39	7.58	7.31	1.92	19.2	2
36	6.64	6.43	...	30.6	2 −
35	5.76	5.16	1.85	9.75	1+
32	5.66	4.98	...	17.7	1.75 −

The use of nearly monochromatic light effectively eliminates disturbing differences in color between sample and standard. This minimizes the influence of the personal factor of the observer, which is often troublesome in methods using white light, where the effect of both hue and brightness must be evaluated in deciding on a match. The beneficial effect on the precision of matching is illustrated by the following example: Determinations were made of the color of two samples by three observers using (*A*) white light and fixed depth of oil standard and (*B*) green light and fixed depth of oil standard. The average deviation from the mean for all observers on both samples was 2.5 per cent using method *A* and 1.0 per cent using method *B*.

Having shown that a satisfactory color method resulted when samples diluted with benzene were matched against a neutral filter standard in green light covering a narrow band of wave lengths, the next steps were to find a reproducible substitute for the green filter, and a means of calibrating the neutral filter in absolute units. The transmission curve of the green gelatin filter used up to this point is shown in Figure 7.[2]

It was considered that this curve would be duplicated with materials most readily specified and obtained and least dependent on the products of any one manufacturer, if a colored solution was used as filter. Preference was given to inorganic salts, rather than organic dyes, since as a class the salts would be more easily duplicated and more stable with time. A survey of the available literature and an examination of some twenty solutions with a small direct-vision spectroscope resulted in the choice of a 30-mm. layer of a strong solution of

[2] The transmission curves given in Figure 7 were determined by Razek and Mulder, using the Razek-Mulder color analyzer.

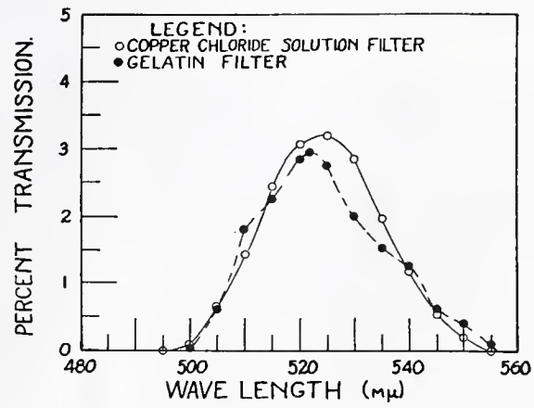

FIGURE 7. TRANSMISSION CURVES OF GREEN FILTERS

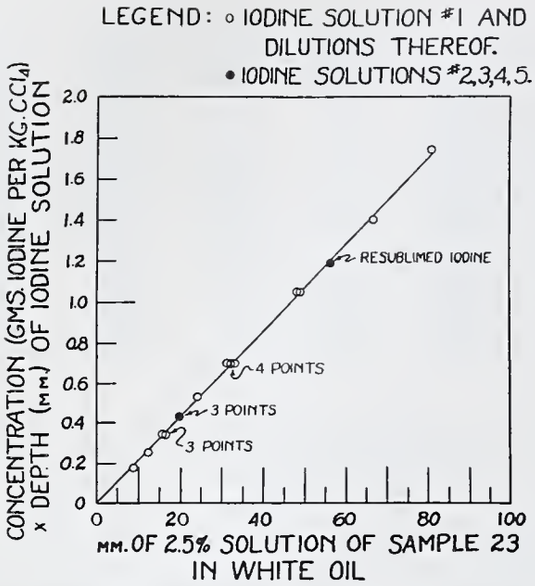

FIGURE 8. PROPORTIONALITY OF OIL COLOR AND IODINE COLOR IN GREEN LIGHT

cupric chloride in water. Figure 7 shows that the transmission curve of this solution in a clear glass cell is a close approximation to that of the gelatin-in-glass filter previously used.[3]

Having found a satisfactorily reproducible substitute for the green filter, the matter of calibrating the neutral filter standard was taken up. A Wratten neutral gelatin filter, cemented between glass flats, was used as working standard in the preliminary tests. For routine tests all-glass neutral filters (supplied by the Bausch & Lomb Optical Company) have been substituted and used satisfactorily in five laboratories. These filters have an optical density of approximately 0.3, but for use in the proposed method they must be standardized more exactly. This is accomplished by comparing them, in the Duboscq colorimeter, with a master standard consisting of a liquid of known optical density per millimeter and which is known to change its optical density linearly with increasing depth. In the search for such a liquid, tests were made of some 28 solutions, with the result that dilute solutions of iodine in carbon tetrachloride were found to obey Beer's Law in the light passed by the authors' green filter. Figure 8 shows that when a solution of sample 23 is matched against such solutions, a linear relation is found between the depth of the oil solution and the product of the depth and concentration of the iodine solution. The satisfactory reproducibility of the iodine solution is also demonstrated by the points plotted from data on the several solutions. Since Brode (*2*) and Getman (*6*) have published data on the spectral transmission of solutions of iodine in carbon tetrachloride, the optical density of such solutions can be calculated for given depths and thicknesses if the energy distribution throughout the spectrum of the illuminant is known. A discussion of calculations of this kind is given by Davis and Gibson (*4*). Figure 9 shows the relation between the optical density per centimeter and the concentration for solutions of iodine in carbon tetrachloride. It must be emphasized that the optical densities read from Figure 9 will be correct only when the solution is viewed in the illumination furnished by the green filter specified in Figure 7, in combination with a source of 1850° K. color temperature. Use of a filter with a different transmission curve might result in appreciable differences in optical density of the iodine solution. The calculations are not so sensitive to changes in color temperature of the source, since a recalculation based on a color temperature of 2600° K. for the source made only 1 per cent difference in the optical density figures. From the equation of the line shown in Figure 9, the optical density D (in the green light) of a neutral filter which is matched by X mm. of an iodine-in-carbon tetrachloride solution of concentration C mg. per liter is given by

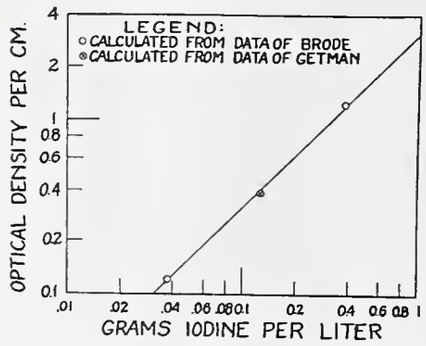

FIGURE 9. OPTICAL DENSITY OF SOLUTIONS OF IODINE IN CARBON TETRACHLORIDE

Used in green light colorimetry.

$$D = 0.0003193 \times (\text{mg. iodine per liter}) \times (\text{depth in mm.}) \quad (2)$$

In order to express color values in more fundamental units and to differentiate between color determined by this method and by any of the older true color methods, the unit of the scale has been chosen as 1000 times the optical density per millimeter thickness of sample and the name optical density (O. D.) scale has been assigned to the new scale. Then if, in a determination, R mm. of a given oil sample match a neutral filter of optical density D, the optical density color of the oil is 1000 D/R.

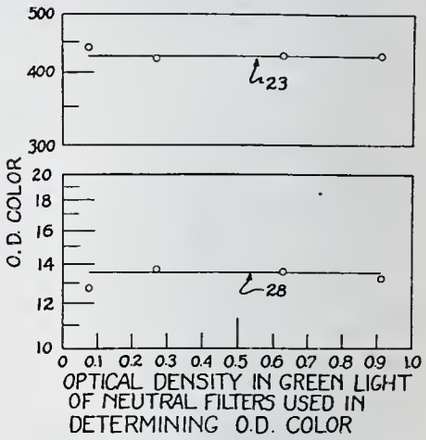

FIGURE 10. OPTICAL DENSITY COLORS DETERMINED IN GREEN LIGHT

Neutral filters of several densities.

A comparison of several of the true color oil standards used in the method of Weir, Houghton, and Majewski (*12*) with a neutral filter calibrated for density has permitted the generalization that the following relation exists between true colors determined by their method and optical density colors

$$\text{Optical density color} = 1.57 \times \text{true color} \quad (3)$$

One of the disadvantages of the true color method using white light and oil standard was that it led to different color values if the depth of standard was changed. The method herein presented gives the same color values for any optical density of standard within the practicable working range. This is shown in Figure 10, where the optical density colors of one light and one dark oil remain constant regardless of the density of the neutral filter used in the determination. The points for the filter of lowest density are considered reasonable checks in view of the increased uncertainty in the determination of the density of this filter.

A detailed description of the method is given below. When it is followed exactly, the accuracy obtained is comparable to any photometric method, check determinations by several observers agreeing to within 2 per cent of the average. Under routine conditions, with identical samples distributed monthly by a control laboratory, four laboratories have consistently reported results within 5 per cent of the average.

[3] Tests are being conducted on glass color filters of a size to be conveniently slipped into the Duboscq eyepiece, but because of its reproducibility from specifications, the cupric chloride solution filter is considered as standard.

Determining Additive Colors on Optical Density Color Scale

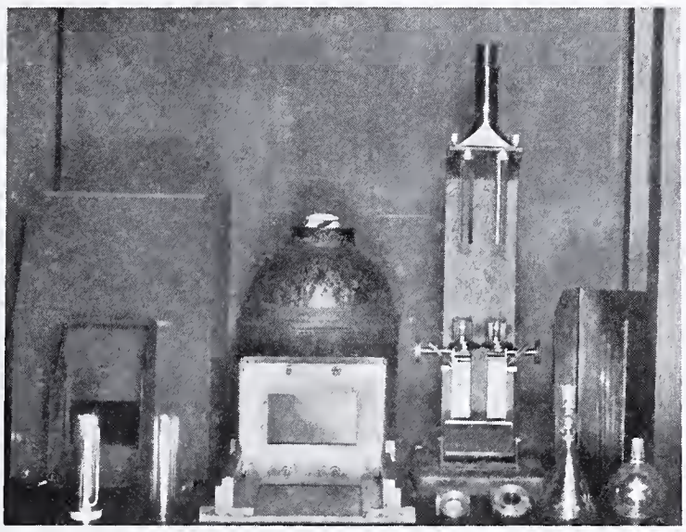

Figure 11. Colorimeter and Auxiliary Apparatus for Determination of Optical Density Colors

Set-Up of Machine. The determinations should be carried out in a room which is completely dark except for the small light leakage from the instrument. Preferably, the entire room should be painted a dead black, and should be small enough to exclude other work or the presence of more than two men at a time. It is essential that the wall facing the operator, as he sits at the color machine, be nonreflecting. In locating and installing such a colorimeter room, proper ventilation should be provided and underground steam lines avoided as much as possible.

A table or stand for the instrument and stool for the operator are provided, of such relative heights that readings may be made without undue strain.

A Bausch & Lomb Duboscq colorimeter No. 2504, 100 mm., and Bausch & Lomb colorimeter lamp No. 2414 have been found satisfactory for this test. Purchasers of new instruments should specify that the Duboscq plungers be cemented in place with benzene-proof cement. The colorimeter with its removable shield is shown on the right of Figure 11.

For routine testing the oil to be examined is placed in a cup 25.4 mm. (1 inch) in diameter and 108 mm. (4.25 inches) deep, the bottom of which consists of a disk of optical glass sealed to the bottom of the tube with benzene-proof cement. When relatively few determinations are to be made, the cups furnished with the colorimeter suffice. Both types are shown in Figure 11 (left front).

A 60-watt, inside-frosted Mazda bulb is specified.

A distinctive feature of this procedure is that matches are made with use of green light, which is secured by placing between the light source and mirror of the colorimeter a glass cell containing a green solution. The solution in use at present is made by dissolving 326.0 grams of Baker's c. p. cupric chloride ($CuCl_2.2H_2O$) and 0.50 gram of Baker's c. p. mercuric chloride in 351.3 grams of distilled water and filtering once through Whatman No. 42 paper. The solution is contained in a glass cell such that the light passes through 30 mm. of solution. The cell specified for this purpose is a metal-glass-Bakelite cell using rubber gaskets instead of cement and made to order by the Arthur H. Thomas Company. (Duplicates may be ordered by referring to A. H. Thomas blueprint 587.) If this cell is used, the solution gradually darkens and should be replaced monthly. An alternative cell, which is more fragile but which does not darken the solution, is Arthur H. Thomas Company No. 9173, 100 × 100 × 30 mm. (3.9375 × 3 9375 × 1.1875 inches). If this cell is used the cover is sealed on with Canada balsam to prevent evaporation. The take-down cell is shown in Figure 11 in front of the colorimeter lamp.

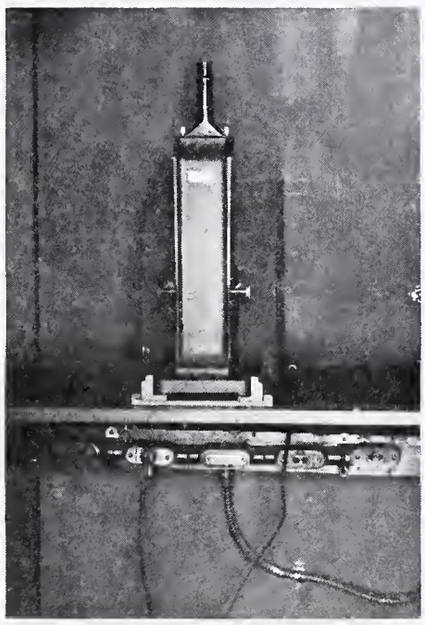

Figure 12. Assembled Apparatus for Determination of Optical Density Colors

In order to introduce the cell into the light path the illuminator housing, baseboard, and light-tunnel must be cut back. The manner of doing this will be apparent from Figure 11.

In order to prevent any light from reaching the Duboscq mirror other than that which has passed through the green filter, a light screen is used, which also shields the eyes of the operator from stray light. Such a shield is shown in Figure 11 (left rear).

The working standard in this procedure is a 25.4-mm. (1-inch) square glass neutral filter. This is introduced into the system by replacing the left hand cup of the Duboscq by a specially made brass mounting which holds the neutral filter and a glass equivalent to the bottom of the removed cup.

Neutral filters are pieces of gray glass about 25.4 × 25.4 × 3.0 mm. (1 × 1 × 0.125 inch), with an optical density of about 0.3. They are calibrated and issued by the control laboratory and periodic rechecks are made. Reasonable care must be exercised in handling these filters. They should be cleaned, if necessary, by wiping with soft lens paper. They must not be washed with solvents of any kind, nor scratched by rubbing with a gritty cloth.

In order to introduce the neutral filter and the special cup into the set-up, brass adapters are used. These are shown in Figure 11, propped up in front of the Duboscq colorimeter. Figure 12 shows the apparatus completely assembled.

Preparation of Sample. Oils which, in depths of from 8 to 90 mm., match the standard neutral filter need no further preparation.

Haze due to small quantities of suspended matter in the oil must be removed by filtering before taking the color. If this is not done the grayness imparted by the haze will be read as color and lead to erroneous conclusions for ordinary purposes. (This applies to haze produced by suspended salts, water, or small quantities of separated wax.)

Dark oils which flow readily are to be diluted with benzene of 30 Saybolt color in the ratio of one volume of oil to 10 volumes of solution. If this solution is still too dark to match the neutral filter at a depth greater than 8 mm., a second and if necessary further dilutions should be made, always in the 10 to 1 ratio. These dilutions are to be made in a special flask calibrated at two points so that the volumes indicated have a ratio of 9 to 10; and with volume between the two marks of 10.0 ± 0.05 ml. The flask is to be

closed, while mixing, by a special bulb-type stopper with ground-glass joint, and not by cork or operator's thumb. The bulb-type stopper permits completion of mixing before transfer. Pyrex flasks of this type can be obtained from the Corning Glass Company. The flask and bulb-type stopper are shown in Figure 11 (right front).

The benzene used for the above dilutions should be steam-distilled and filtered through paper before use.

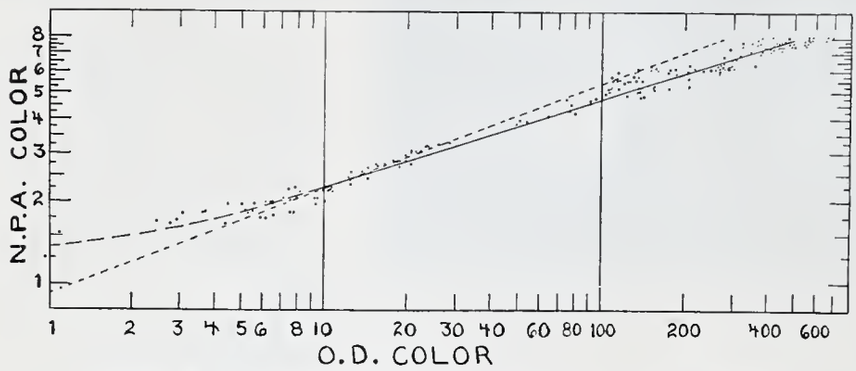

Figure 13. National Petroleum Association and Optical Density Color Data for Various Samples

Dark oils too viscous to flow readily and oils of high pour may be warmed sufficiently so that they will pour and then added to the benzene in the dilution flask, stopping a little short of the second mark. After the contents of the flask have cooled to room temperature the volume is adjusted to the mark by adding the necessary few drops of solute.

Taking the Color. The following parts are examined and cleaned if necessary: 2 plungers, cup on right side of machine, bottom glass and neutral filter on left, mirror (silvered side), large surfaces of green filtercell, bulb in illuminator, and inner reflecting surfaces of bulb housing, particularly the bottom. It will also be necessary occasionally to remove dust from the top section of the eyepiece which can be unscrewed for that purpose.

The clean cup is now placed on the right side of the instrument and the filter holder, without the filter but with the bottom glass, on the left. The light shield furnished with the machine is put in place, the light turned on, and the field observed. The eyepiece tube should be pushed in or out until the line of separation between the two sides of the field appears sharpest to the observer making the test. Both sides should appear equally bright. If they do not, then either the cleaning was inefficient or the optical system is out of balance. If the field appears equally bright on both sides, the cup on the right is racked up until the plunger touches its bottom. The scale on the right should now reach zero, and should be adjusted to do so if necessary. The neutral filter is placed in position in its holder, which is racked up until the plunger and neutral filter are nearly in contact.

The oil or solution to be tested is placed in the cup, which is then replaced on the right of the machine and racked up and down until the fields match in intensity. The eye should be held as nearly as possible on the axis of the eyepiece while matching, and the point of match should be approached from both sides by "bracketing." Six readings of the depth of match should be taken and averaged. However, on starting a series, it is well to discard the first few readings so as to give the eye time to adjust itself. If the average reading is below 8 mm., another set of readings should be taken on a more dilute sample. After each sample the cup and plunger should be washed with benzene and volatile naphtha. For this purpose a test tube which can be half-filled with solvent and then slipped up around the plunger eliminates the necessity of wiping the cup or plunger except occasionally.

Calculating the Color. Color values on the optical density scale are calculated from

$$\text{Optical density color} = \frac{10^3 D \times 10^N}{R} \qquad (4)$$

where D = optical density of neutral filter

$= \dfrac{\text{log incident light}}{\text{transmitted light}}$

R = mm. depth of oil (or solution) to match neutral filter

N = number of dilutions (in 1 to 10 ratio)

These color values are named optical density colors (colors on the optical density scale) because they are calculated from the depth of oil (or solution) having an optical density equal to that of the neutral filter working standard. The neutral filters as purchased are not accurately calibrated and hence must not be used until a calibration has been supplied by the control laboratory. To illustrate the calculation in a few specific cases the following examples are given:

(1) Oil Not Requiring Dilution. Density neutral filter = 0.336 = D. Depth of undiluted oil to match = 12.0 mm. = R.

$$\text{Optical density color} = \frac{10^3 \times 0.336}{12.0} = 28.0$$

(2) Oil Requiring Dilution. Same neutral filter, D = 0.336. Depth of solution at match = 27.0 mm. = R. Number of 1 to 10 dilutions = 2 = N.

$$\text{Optical density color} = \frac{10^3 \times 0.336 \times 10^2}{27.0} = 1244$$

Since the measurements are uncertain in the third figure, this result should be written 1240.

(3) Dilution Flask Not Exactly 1 to 10 Ratio. If the dilution flask used does not give exactly a 1 to 10 ratio the following formula is used:

$$\text{Optical density color} = \frac{10^3 D \times (\text{dilution factor})^N}{R} \qquad (5)$$

For example: Density of neutral filter = 0.336.

$$\text{Dilution factor} = \frac{\text{volume of solution contained by flask}}{\text{volume of oil taken for dilution}} = 9.70$$

Number of dilutions = N = 2. Depth of final solution at match = 38.0 mm. = R.

$$\text{Optical density color} = \frac{10^3 \times 0.336 \times (9.70)^2}{38.0} = 832$$

Relation of O. D. Color to N. P. A. Color

Figure 1 demonstrated that, comparing two oils in white light, various results may be obtained, depending upon the thickness of oil layer. Nor is this a phenomenon connected with a colorimeter of the Duboscq type. Samples 1 and 2 were placed in tubes of various diameters. In tubes of 2 to 5 mm. diameter, sample 2 was unquestionably lighter, although in 35-mm. tubes (4-oz. bottles) it was just as definitely darker than sample 1. N. P. A. color is, then, comparable to a white-light true color at a fixed depth (35 mm.), and since the optical density color eliminates this variation of color with depth, no strict correlation between N. P. A. and optical density color is possible.

That there is a rough correlation is demonstrated by Figure 13, which contains values for 190 diverse oils. The solid line between 2 and 8 N. P. A. was determined on another series of oils. Below 2 N. P. A. (broken line) the line seems to depart from linearity, which appears to be in agreement with (unpublished) color analyses of N. P. A. standards which reveal that below 2 N. P. A. the interrelationships between standards are of a different nature than those between the standards from 2 to 8 N. P. A.

The dotted line corresponds to that of Weir, Houghton,

and Majewski (*12*) for true color. It is not in good agreement with the data for the wide variety of oils included here, but there is evidence that it is valid for light distillates, finished by acid-treating alone, which was the type of oils considered by them.

ACKNOWLEDGMENT

Acknowledgment is due to H. M. Weir, who brought the advantages of the true color system to the authors' attention; to M. L. Wood for preliminary work on the problem and the suggestion of using monochromatic light; to W. F. Houghton, A. B. Guise, and S. S. Kurtz, Jr., for helpful discussion; to K. O. Brown and J. A. Kane who made many of the determinations during the development period; and to the many laboratory technicians who have assisted in making this method a success in routine work.

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Inverted Fractional-Distillation Analysis

Inversion Column

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A description is given of a rectifying apparatus for normal pressure, which allows analysis by distillation of mixtures of gases or liquids, commencing with the components with the highest boiling point.

The apparatus has a range of about +200° to −170° C.

The fractions can be collected in liquid or in gaseous condition, as desired.

The analysis can be terminated at any point, which shortens the duration of the analysis considerably in many cases, especially when determination of the fractions with the highest boiling points is of chief importance, which frequently happens in the petroleum industry.

FOR the continuous splitting of a mixture of components—for instance, by distillation or extraction—when use is made of the difference in the coefficient of distribution of the components over two phases, three chief types are distinguishable. In the case of distillation these are (1) flash distillation, (2) rectifying dephlegmation, and (3) complete rectification.

In the first case the mixture is divided over two phases, which are then separated from each other. In the second case the mixture is introduced on one side of the column, while part of the product escaping on the other side is re-fed in another phase as reflux, which after being interchanged in the column flows away on the first side. In the third case the mixture to be split is introduced into the middle of the column. The column may here be looked upon as being constructed of two halves, each working according to the second type. It is of importance that the two phases in these two halves play an opposite part.

For the discontinuous separation, applied for analysis, three analogous cases are conceivable. The first is closely connected with analytical distillation, such as the A. S. T. M. distillation (D86-30); the second, with analytical rectification for distillation, as with the Podbielniak apparatus (*1*); the third case is also imaginable to a certain extent.

For the usual fractional-distillation analysis of the second type, the mixture to be separated is, as a rule, introduced as vapor at the bottom of the column, so that the lightest component is the first to be separated as the top product. It is, however, just as possible to introduce the mixture as liquid at the top of the column, in which case the heaviest component is the first to be separated as the bottom product. This can also be expressed as follows: The reflux can just as well be a gas phase as a liquid phase, as was demonstrated with the apparatus for absorption analysis (*2*). In principle, this is much more logical in many cases, as for example, when the main interest in the analysis is in the quantity of the heaviest components, which is frequently the case in the petroleum industry. In the usual rectification by boiling point—e. g., Podbielniak apparatus—the lightest component is conveyed to the column in a relatively high concentration, owing to the partial evaporation of the trial sample. Similarly, when the phases are interchanged, it should be attempted artificially to realize a feeding of a liquid with a high concentration of the heaviest components. In the following pages the apparatus required for this method is described in detail.

THE TOP COOLING

The trial sample, in the liquid phase, is in reservoir H (about 50 cc.), from which it continuously flows, through capillary C in the bottom, into column K_2 which is packed with glass rings (Figure 1). This is electrically heated (V_2), so that only an adjustable part flows down into the rectifying column K_1. The part evaporated in K_2 rises through a separate tube S above the liquid reservoir, but it is there continuously condensed, by a top cooler D-E of great capacity, and re-fed to the liquid reservoir. The cooling liquid in the top cooler depends on the mixture to be separated; for the analysis of gases rich in methane it is liquid nitrogen.

In order to maintain a normal pressure in the whole apparatus,

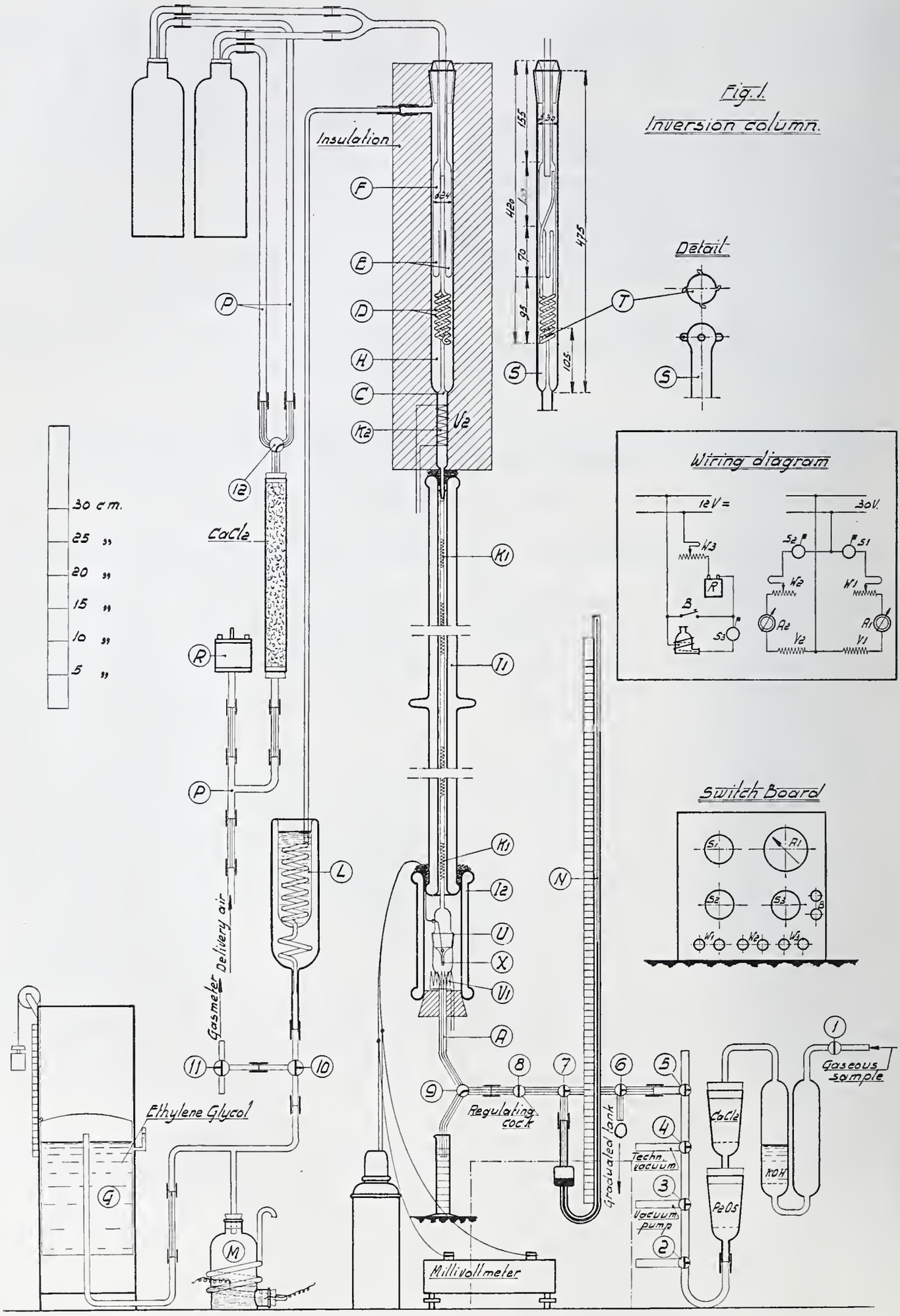
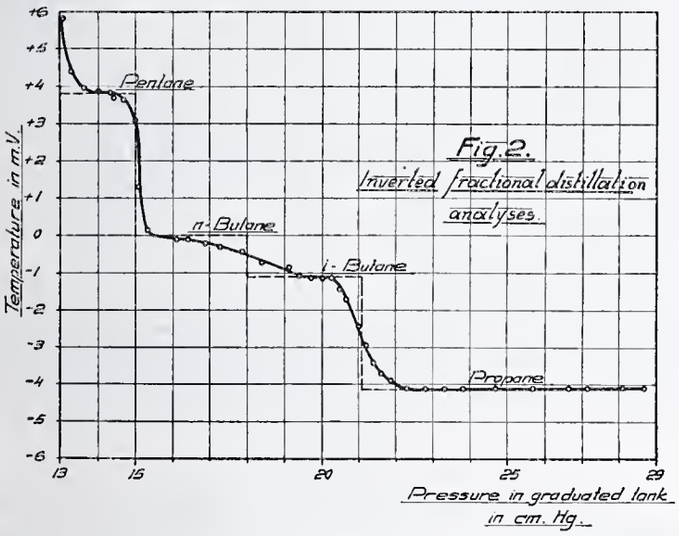


Fig. 1.
Inversion column.
Insulation
Detail
Wiring diagram
12 V =
30 V.
Switch Board
30 cm.
25 „
20 „
15 „
10 „
5 „
CaCl2
Delivery air
Gasmeter
Ethylene Glycol
Regulating cock
Graduated tank
Techn. vacuum
Vacuum pump
Millivoltmeter
Gaseous sample
CaCl2
KOH
P2O5

the space around the top cooler is connected with gas tank G (capacity about 2 liters), filled with a noncondensing gas (hydrogen) above ethylene glycol (low vapor pressure, slight solubility of hydrogen or hydrocarbons). This gas also surrounds the top cooler, in so far as it is not driven out by the condensing vapor. This makes it possible for the condensation level to rise or go down in connection with fluctuations in cooling, etc., constant pressure (2 cm. water of excess pressure) being guaranteed by the gas tank.

The condensation normally takes place at the cooling coil D, which is continuously filled with liquid nitrogen from the cooling vessel F. As soon as the stock in this vessel is exhausted, the condensation level rises to the test tubes E, which are now only just filled.



The accompanying expulsion of hydrogen to the gas meter is utilized in the contact manometer M to close an electric current. This closes in the relay R the outlet of the compressed air tube P. The current of compressed air, limited by capillaries, now presses the liquid nitrogen from one of the thermos flasks into the cooling vessel. Owing to this, the condensation level drops again and the expelled hydrogen reënters, passing through the Dewar tube L, in which, at $-20°$ C. (ice and salt), the vapor of the ethylene glycol from the gas tank is sufficiently precipitated.

This automatic supply of nitrogen proved, in all the experiments, to insure a perfectly regular circulation of liquid and vapor above the rectifying column, entirely independent of the moistening of the column and the collection of the liquid regulated by the manipulator.

Some tentative experiments brought to light two difficulties in the required transmission of much heat: The rising vapor is easily cooled down so far that a stable, dense mist is formed; the mist drops may even pass the cooler. Also, too high a percentage of high-boiling constituents should be avoided, on account of the risk of freezing out at the cooler.

In the construction employed, these components are sufficiently removed from the vapor by a rectifying interchange in the top column K_2 and by dephlegmation on the wall of tube S in which the evaporated part rises. The vapor is then made to rotate strongly by the sprayer T near the cooling coil, by which the mist formed is effectively centrifugalized. Moreover, the temperature on the wall of the (double-wound) cooling coil is adjusted to some extent, as the nitrogen vapor developing in it constantly prevents it from being entirely filled with the cooling agent. The difference in height between the two ends of the coil in the cooling vessel F acts like a gas-lift pump and causes the nitrogen to circulate through the coil.

Rectifying and Measuring Apparatus

In order to render the results as comparable as possible, the rectifying column K_1 was chosen in exactly the same shape as that used by Podbielniak in his apparatus (inside diameter 4 mm., length about 80 cm., wire coil packing); it is also surrounded by a silvered vacuum jacket I_1.

At the bottom the column ends in a wide ground joint U, the inside of which ends in a very thin-walled, narrow tube. In this are suspended the three thermoelements X. The liquid dropping down through it falls in drops onto the aperture of the discharge capillary A, which is heated by the heating device V_1. The vapor formed returns to the column through openings immediately above the thermoelements.

The circulation of air in the (unsilvered) vacuum jacket I_2 causes part of the dripping liquid to evaporate before it reaches the thermoelements, so that an excessive supply of heat to the capillary aperture can be avoided. This would easily give rise to errors in the reading of the temperature, owing to heat radiation to the thermoelements.

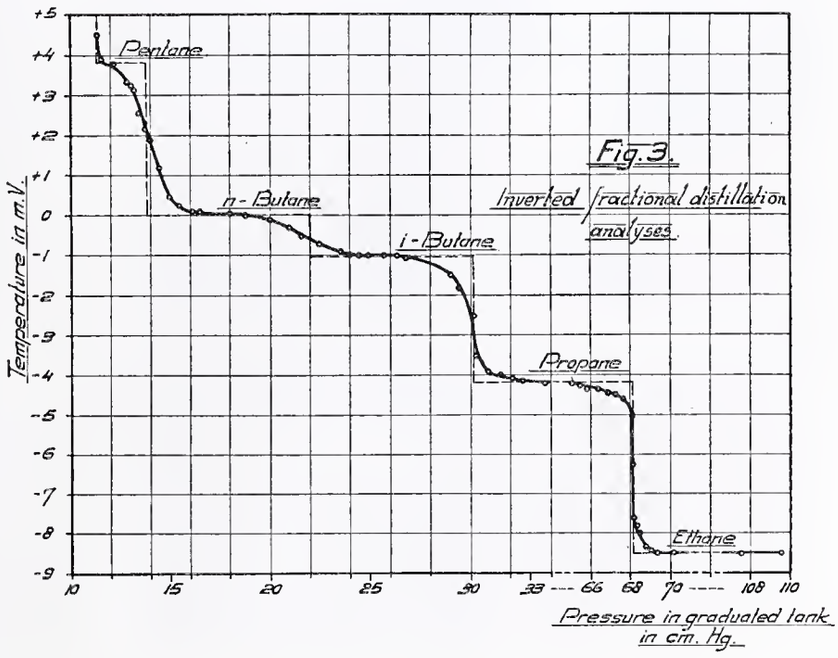
Through the very narrow discharge capillary A and the drain cock 9 the rectified product can be collected, as desired, as liquid in a graduated cylinder or as gas in the graduated tank O, the pressure in which is registered by the barometer N, which is closed on one side. (Tight shutting of cock 9, also after the liquid has passed, is insured by the use of gasoline-insoluble cock grease, such as "Resistol."

Tank O can be evacuated by the prevacuum tubing and the vacuum pump, connected at 4 and 3. To this cock manifold is also connected the feed tube for the gas sample 1, which is freed from possible carbon dioxide and dried in the wash bottles indicated.

The Analysis

Before the analysis is started, the gas tank G is filled to about one-fourth, through cocks 10 and 11, with carefully dried hydrogen. The column is also rinsed and filled with hydrogen, before being connected with the gas tank. In the case of a light product, the top cooler is filled with liquid nitrogen, for which purpose the compressed air relay R is made to function by press button B (see wiring diagram). About 250 cc. of hydrogen then pass from the gas meter to the column.

A gaseous sample is introduced (after rinsing out the wash bottles and the cock manifold up to cock 5) through cocks 1 to 9, inclusive. About 100 cc. of hydrogen are driven out of the column by this. Immediately after this slight rise in the gas tank (during intense cooling), its reading should be noted. The feed of gaseous sample may now be increased to about 1.5 liters per minute. If the sample also contains hydrogen, oxygen, nitrogen, or the inert gases helium or argon, these will join the hydrogen present while the sample is introduced;



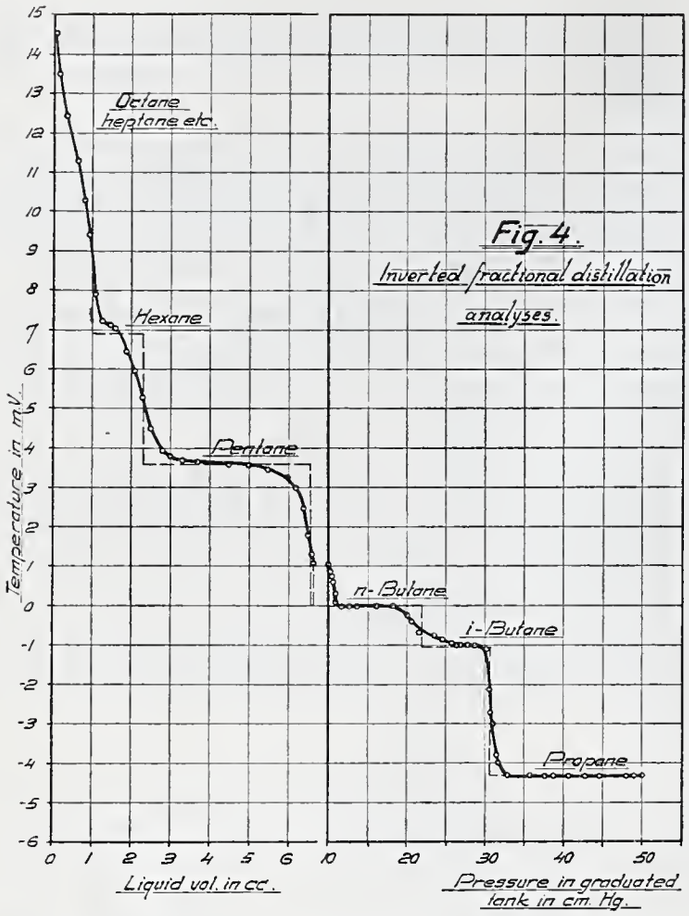


Fig. 4. Inverted fractional distillation analyses.

their volume is determined by reading the rise in the gas tank during the introduction. If this is more than 1 liter, a known volume can be quickly withdrawn from the gas tank through cocks 10 and 11. A concentration of oxygen of more than 10 per cent in the gas tank should be avoided because of condensation, which results in a strong development of mist and irregularity in the cooling.

If a liquid sample has to be introduced, some methane plus ethane (about 5 liters) should first be put in as conveyor gas for the top circulation to prevent freezing of the high-boiling components on the cooling coil. The liquid sample can subsequently be introduced under some excess pressure from the flask through the liquid draining capillary.

After introducing the trial sample, the drain cock is closed, the automatic cooling regulation is switched in, and the heating device V_2 is so adjusted as to prevent the propulsion of liquid in the column. By means of the heating device V_1 the manipulator regulates the wetting of the aperture of the discharge capillary.

During the further execution of the analysis, the manipulator's care for the cooling is restricted to the regular switching in of a full thermos flask (cock 12) and to refilling the empty one. The regulation of the column load (heating device V_2) only rarely requires attention, which is occupied in securing the right degree of moistening of the thermo-elements.

This differs from the Podbielniak apparatus in that a possible liquid propulsion at a low column temperature occurs mostly, if at all, far from the measuring point—at the top of the column—and has only an indirect influence on the rectification.

When the heating by V_1 is gradually increased, the temperature registered by the millivoltmeter is first seen to rise slowly and then, all at once, to a very great extent. The former movement is caused by the lower boiling components being forced back to the column, the latter by the drying out of the thermoelements. These should be kept just sufficiently moist, which requires less supply of heat in proportion as more rectificate is exhausted.

Reflux Ratio. In the butane range (slight exchange of heat with the surroundings) the charge of the heating device V_1 was about 10 watts, equivalent to 2.4 gram calories per second (Figure 2). This means (molecular heat of evaporation of butane equals 5400 gram calories per gram molecule) a reflux of about 0.00044 gram molecules per second or about 10 cc. of gas per second.

The rate of flow to the graduated tank was about 0.28 cc. of gas per second. The ratio of reflux was therefore about 40.

Attention should here be drawn to the possibility afforded by this apparatus of adequate checking of the ratio of reflux at the drainage end of the rectifying column, whereas as a rule this ratio is known only for the other end of the column.

As with the Podbielniak apparatus, the analysis is recorded by noting the values observed simultaneously for the volume of gas (or liquid) discharged and for the temperature registered by the millivoltmeter. If the discharge is regular, the temperature can be read at any moment, in contrast with the Podbielniak apparatus.

When the analysis has been continued long enough, or when the lowest-boiling component has been reached, drain cock 9 is closed and the column is connected by cocks 10 and 11 with a gas meter. The automatic cooling is disconnected. The remaining gas then escapes through the gas meter at the rate of about 2 liters per minute.

Examples

In Figures 2, 3, and 4 the values found in trial analyses have been plotted. The millivoltage of the thermoelements

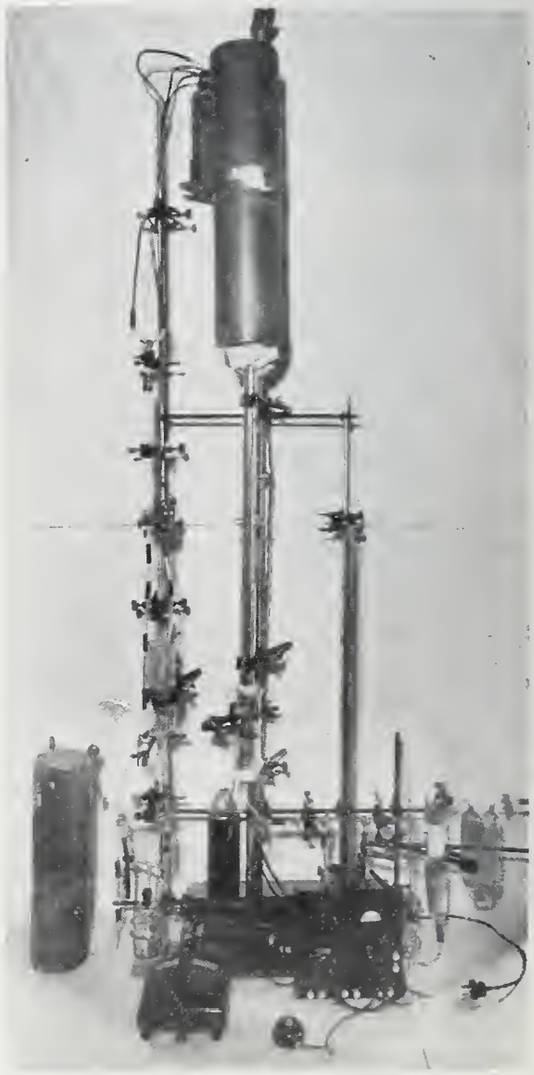


Figure 5. Bosschart Inversion Column

has in each case been taken as the ordinate (1 millivolt equals about 10° C.), the abscissa indicating the pressure in the graduated tank (or the volume of liquid drawn off).

Figure 2 represents a brief analysis of the top gas obtained in the industrial production of gasoline. The trial sample (about 15 liters) was introduced in about 20 minutes. The regulation of the heating took 15 minutes, the rectification itself 1 hour, hence the whole analysis took over 1.5 hours.

The product was measured exclusively in the gaseous condition.

Results of Determination. Rise in the gas tank during the introduction was 6.0 cm. Increase in pressure in the graduated tank while the separate components were rectified off (Figure 2) was:

	Mercury
	Cm.
Initial reading of barometer	13.0
For pentanes and higher components	2.0
For normal butane	3.0
For isobutane	3.1
For propane	7.6
Final reading of barometer	28.7

The quantity of gas (methane plus ethane plus propane) which subsequently passed through the gas meter (converted to dry gas at 20° C.) was 12.61 liters.

The measuring apparatus is so calibrated that 1 cm. rise in the gas tank gives an increase of 116 cc. of gas, and 1 cm. mercury rise of the pressure in the gas tank gives an increase of 71 c. of gas.

Table I. Analysis of Top Gas

Component	Gas	Per Cent by Volume: Bosschart apparatus	Per Cent by Volume: Podbielniak apparatus
	Cc.		
Pentanes and higher (2.0 × 71)	142	1.0	1.1
Normal butane	213	1.5 }	3.2
Isobutane	220	1.5 }	
Propane	>540	>3.7	6.7
Ethane plus methane	<12610	<87.5	84.5
Oxygen, hydrogen, nitrogen, etc. (6.0 × 116)	696	4.8	4.5
Total	14421	100.0	100.0

Carbon dioxide, if present, should of course be determined chemically, like the composition of the noncondensable part.

Figure 3 shows a similar sample from the same plant, a trial sample about 45 liters. The analysis has been continued further. The duration was:

	Min.
Introduction of sample	40
Establishing of equilibrium	15
Time of distillation	3 hours
Total, about	4 hours

Table II. Continued Analysis of Same Top Gas

Component	Increase in Pressure[a]	Gas	Per Cent by Volume
	Cm. Hg	*Cc.*	
Pentanes and higher	2.4	171	0.4
Normal butane	8.2	582	1.3
Isobutane	8.1	575	1.3
Propane	38.1	2,710	6.1
Ethane	>41.4	>2,940	>6.6
Methane (gas meter reading, converted)		<37,320	<83.2
Noncondensable (= 4.3 cm. rise in gas tank)		499	1.1
Total trial sample (rounded off)		44,800	100.0

[a] According to Figure 3.

Figure 4 represents the analysis of a gas which still contains gasoline. As the higher-boiling components have been collected and measured as liquids (left half of Figure 4), all the data have been converted to weight. The duration was:

	Min.
Introduction of sample (about 20 grams)	25
Establishment of equilibrium	20
Rectification	3.5 hours
Total, about	4.5 hours

Table III. Analysis of Gas Containing Gasoline

Component		Volume of Liquid	Specific Gravity Gas			Per Cent Weight
		Cc.	*Cc.*		*Grams*	
Drawn off as liquid						
Heptanes and higher		1.0	0.70		0.70	3.5
Hexanes		1.3	0.66		0.86	4.3
Pentanes (grad. cyl. 0° C.)		4.2	(0°) 0.65		2.74	13.9
Normal butane (grad. cyl. 0° C.)		0.1	(0°) 0.60	(0.06)	2.20	11.1
		Gas Volume	Liter Weight			
Drawn off as gas	*Cm. Hg*	*Cc.*[a]	*Grams/l.*			
Normal butane	12.1	800	2.67	(2.14)		7.8
Isobutane	8.8	583	2.67		1.55	>13.1
Propane	>19.5	>1290	2.02		>2.60	
Methane plus ethane (gas meter reading)		<8520	abt. 1.0		<8.52	<43.2
Noncondensable (rise of gas tank 4.1 cm.)		444	abt. 1.4		0.62	3.1
Total weight of trial sample about					19.80	100.0

[a] Converted to 0° C.

Conclusion

The apparatus described makes it possible to rectify mixtures of gases or liquids at boiling points between +200° and −170° C.

Especially when chiefly the higher-boiling components have to be determined, or when the lowest-boiling component strongly preponderates in percentage, the analysis can be finished in a very short time.

Other advantages are simple regulation and sharp control of the exact moistening of the thermoelements, adequate control of the ratio of reflux, and reduction of the dead space. Between the place where the temperature is registered and that where the volume is determined the formation of liquid is greatly restricted.

Since all the systematic deviations must be about equal but opposite to those occurring with the Podbielniak apparatus, a careful comparison of the two methods on the same sample will afford a long-sought-for opportunity of surveying and eliminating these deviations.

Acknowledgment

The author wishes to express thanks to the N. V. De Bataafsche Petroleum Maatschappij for allowing publication of this article, and to the staff of the Amsterdam laboratory, especially to R. N. J. Saal, for their readiness to lend their assistance.

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New Norwegian Process for Manufacture of Sodium Nitrate. Details in connection with the new process for manufacturing sodium nitrate recently developed in Norway have just been given out, according to a report made public by the Commerce Department.

The process, which will be patented in all important countries, is based on the use of artificial zeolites. Seawater somewhat concentrated is pumped through a large container filled with a calcium base-exchange medium. When the reaction has occurred the sodium zeolite is treated with a concentrated solution of calcium nitrate, resulting in the formation of sodium nitrate and a calcium zeolite. Seawater is again introduced and the process repeated.

The sodium nitrate produced by this process, the report states, is not much more expensive than the calcium nitrate now being produced, especially if it is considered that sodium nitrate can be packed and shipped in much cheaper sacks. The new product is stated to be practically the same as natural sodium nitrate and it is alleged that the synthetic can compete with the natural in price.

Qualitative Method for Selenium in Organic Compounds

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WHEAT plants grown by the Bureau of Plant Industry at the Arlington Experiment Farm on normal soil to which had been added from 1 to 20 parts per million of selenium in the form of sodium selenate were believed to contain small quantities of selenium. Only a limited supply of these plants was available for analysis, and a quick method which would require only a gram or so of material was desired to test this material for selenium.

The method of Schmidt (*3*), used by Stover and Hopkins (*4*), seemed to be the quickest procedure available.

These workers digested powdered, dried leaves with 10 cc. of concentrated nitric acid until only 2 or 3 cc. remained. This operation with nitric acid was repeated. Then 5 cc. of sulfuric acid were added and the mixture was boiled, a few drops of nitric acid being added from time to time to hasten the oxidation. When a straw-colored solution was finally obtained, the boiling was continued until dense white fumes were evolved. The solution was cooled and brought up to definite volume and 0.01 gram of codeine was added. The presence of selenium was indicated by the formation of a green color, changing gradually to a blue-green and finally to a pure blue color.

The disadvantages of this method are (1) the possibility of losses of selenium on digestion with nitric acid, (2) the difficulty of removing all traces of the nitric acid, and (3) the time consumed in first digesting the material with nitric acid and then removing the nitric acid with sulfuric acid. It is necessary to remove all traces of nitric acid in the digest; otherwise a deep red color is obtained when codeine is added. It was desired, therefore, to eliminate the use of nitric acid if possible, and the Kjeldahl digestion method for nitrogen determination offered possibilities. Besides giving a smooth, quick method of oxidizing the organic material, digestion of the material with sulfuric acid and mercuric oxide offered advantages in the probable formation of a double salt of mercruy with selenium, which lessens the possibility of a loss of selenium by volatilization, and in the change of the inorganic salts occurring in the plants to a state of oxidation that does not give a blue color with codeine.

Lyons and Shinn (*1*) showed that added salts, such as mercuric chloride and zinc chloride, appear to form a double salt with the selenium holding it in solution. Schmidt (*3*) showed that ferric iron in quantities of 1 drop of strong ferric chloride solution in 10 cc. of concentrated sulfuric acid will interfere with the test.

Weighed quantities (0.01 gram) of metallic selenium were digested for 1 hour with concentrated sulfuric acid and a little mercuric oxide, after the manner of Kjeldahl nitrogen digestions. The sulfuric acid digest was cooled and made up to 50 cc. with concentrated sulfuric acid. An aliquot of 5 cc. was taken and 4 drops of a 3 per cent aqueous solution of codeine sulfate were added. The color developed was compared in a Bock Benedict colorimeter against the color similarly developed in a standard solution containing 0.01 gram of metallic selenium dissolved at room temperature in 50 cc. of concentrated sulfuric acid. The standard solution was set in the comparator at 20 mm. The comparison of the color intensities showed that no loss of selenium had occurred during the digestion. Further comparisons made against the same standard with 5-cc. aliquots of the digest diluted 50 per cent and 100 per cent with concentrated sulfuric acid gave the same result.

Two grams of ferric sulfate were digested for 1 hour with 50 cc. of sulfuric acid and mercuric oxide in the manner described. A test of this digest with codeine sulfate gave no blue color, the solution remaining colorless to light yellow.

Solutions were made up with concentrated sulfuric acid containing 0.0005 to 1.0 gram per liter of selenium. These were digested with sulfuric acid and mercuric oxide, and a 5-cc. aliquot of each was tested in a test tube with 2 drops of 3 per cent codeine sulfate solution. All gave visible blue colors, the limit of detection by this method being less than 0.5 part per million.

Plants grown on soil to which selenium had been added and which were known to contain selenium and similar plants grown on normal soil were furnished by the Bureau of Plant Industry. In every test with these plants those known to contain selenium gave a blue color on addition of codeine sulfate solution, while the plants which contained no selenium remained colorless. Tests were then made on wheat straw, corn, wheat flour, wheat leaves and stalks, and soils, only 1 gram of the dried material being used. The test requires no more time than that required for a Kjeldahl digestion for nitrogen.

In order to ascertain just what salts might interfere with this test under the conditions of the experiment, Daniel Ready, of the Bureau of Chemistry and Soils, tested 17 inorganic elements: chromium, nickel, titanium, beryllium, molybdenum, thallium, tellurium, vanadium, boron, antimony, bismuth, arsenic, iodine, manganese, iron, silicon, and tungsten. Only vanadium interfered with the test, giving a dark greenish blue solution on addition of codeine sulfate. Arsenic on digestion with plants gave no color, but on digestion with soils it gave a blue color which rapidly disappeared, leaving the solution a light yellow. There is no evidence that vanadium salts are present in plant material, although they are present in some soils. Ready added 2 mg. of the salt of each element to 5 grams of the soil, and digested the mixture with 50 cc. of sulfuric acid.

This method can be made fairly accurate as a quantitative method if fresh solutions of definite quantities of selenium are made up in sulfuric acid and comparison is made with the unknowns. For quantities ranging from 1 to 5 parts per million it is quite accurate, but when larger quantities are present the color is not permanent. Also, on standing the codeine is gradually acted upon by the sulfuric acid, giving a brown color which interferes with the test. A digest on standing in the open air for several hours absorbs sufficient moisture to interfere with the test. It is of interest to note that the blue color developed by adding 2 drops of codeine sulfate solution in 5 cc. of concentrated sulfuric acid containing 10 parts per million of selenium will gradually disappear if water is added drop by drop. Digests which will not give a test with codeine sulfate, because of absorption of water on standing in the air, can be heated for 15 minutes to distill off the water. The digest will then give the test in the usual way. It is important, therefore, that the codeine be added to the cooled digest as soon after the digestion as possible.

Experimental

One gram of the dried sample is put in a Kjeldahl flask and 40 cc. of concentrated sulfuric acid are added, together with 0.2 gram of mercuric oxide. The mixture is then digested until colorless, and the digest is cooled and made up to definite volume, if desired, with concentrated sulfuric acid. To 5 cc. of the cooled digest in a test tube are added 2 drops of a 3 per cent aqueous solution of codeine sulfate, with cooling and shaking after each drop. If the digest contains selenium, a green color develops

and then rapidly changes to blue. When the method is applied to soils, the cooled digest should be centrifugalized, and the test made on the clear supernatant solution.

Table I shows the results of tests made on samples obtained from the Bureau of Plant Industry. The plus marks denote the relative intensities of color developed by the above test; the figures denote an approximate quantitative estimation made by comparison with fresh standards. All samples taken were 1 gram each in 50 cc. of sulfuric acid. Quantitative determinations made on some of these samples by other methods show the method to be fairly accurate.

Table I. Tests on Wheat Leaves and Stalks Containing Variable Amounts of Selenium

Sample		Qualitative Estimation	Approximate Quantitative Estimation
			P. p. m.
101	Wheat leaves	+++++	20
102	Wheat leaves	++	10
103	Wheat leaves	+	2
104	Wheat leaves	+++++	20
105[a]	Wheat leaves	0	0
106	Wheat leaves	++++++	25
112	Stalks	++++++	25

[a] Sample 105 was grown on soil containing no selenium, the others on soil containing different quantities of selenium.

Table II shows a comparison of substances containing selenium and the normal substance. (R) denotes samples containing selenium determined by Robinson's gravimetric method (*2*).

Table II. Tests on Materials Known to Contain Selenium and Others Known to Contain No Selenium

Straw (R)	Positive
Normal straw	Negative
Corn (R)	Positive
Normal corn	Negative
Wheat (R)	Positive
Normal wheat	Negative
Soil (R)	Positive
Normal soil	Negative

A quick accurate method has been developed for the detection of selenium in organic compounds. The results on samples known to contain selenium and on those containing no selenium are described. Vanadium interferes with the test.

Acknowledgment

The author wishes to express his thanks to A. M. Hurd-Karrer for the numerous samples supplied in connection with this investigation.

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Platinized Silica Gel as a Catalyst in Gas Analysis

II. Oxidation of the Methane Hydrocarbons

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In a previous paper (*3*) it has been shown that the copper oxide tube on the gas analysis apparatus may be replaced by a similar tube containing a commercial platinized silica gel which is an efficient catalyst for the oxidation of hydrogen and carbon monoxide. Hydrogen may be quantitatively oxidized at 100° C.; carbon monoxide acts as a catalyst poison at this temperature, making it necessary to raise the temperature to 300° C. to oxidize the carbon monoxide quantitatively. Although methane is not oxidized at 300° C., nothing is known of the oxidation of ethane and higher hydrocarbons under these conditions. It is common practice to determine hydrogen and carbon monoxide together by oxidation at 300° over copper oxide. In order to determine the possibility of oxidizing hydrogen and carbon monoxide together at 300° in the catalyst tube in the presence of hydrocarbons found in technical gases, the conditions under which methane, ethane, propane, and butane are catalytically oxidized over platinized silica gel were determined.

Apparatus and Gases

The apparatus was that used in the previous work (*3*). The catalyst is the commercial platinized silica gel containing 0.075 per cent of platinum produced by the Silica Gel Corporation for the oxidation of sulfur dioxide to trioxide. Methane was prepared by the action of an alcohol solution of methyl iodide on a zinc-copper couple (*7*). Ethane was prepared by the hydrolysis of ethyl magnesium iodide. The propane was commercial Shellane obtained from the Shell Oil Company and was approximately 97 per cent propane. Butane was prepared by the hydrolysis of butyl magnesium bromide. The hydrocarbons after being prepared were analyzed for hydrocarbon content and then diluted with oxygen before use.

Oxidation of Hydrocarbons

The hydrocarbon-oxygen mixture was passed through fuming sulfuric acid to remove any unsaturates, then over the catalyst at 100° C. to remove any hydrogen. The procedure in using the catalyst tube for hydrocarbon oxidation was exactly the same as that used in the determination of hydrogen. The gas mixture was passed at a rate of 30 to 50 cc. per minute through the catalyst tube heated to the desired temperature. Eight passes were made, as this is in excess of the number needed for the oxidation of hydrogen. The results are shown in Table I.

The results with methane show that it is possible to oxidize hydrogen and carbon monoxide in the catalyst tube at a temperature of 300° C. without oxidizing methane.

The oxidation products from methane and ethane were examined for unsaturated compounds, but none were found. Thus the high ratio of contraction to carbon dioxide is not

due to a dehydrogenation of the hydrocarbon. Adsorption may be one explanation for the larger contraction at the lower temperatures.

It was not found possible to oxidize propane or butane completely, even at a temperature of 400° C.

TABLE I. OXIDATION OF THE METHANE HYDROCARBONS

METHANE					
Analysis	1	2	3	4	5
Heater temp., ° C.	300	325	350	375	400
Contraction, cc.	0.0	0.0	0.0	0.5	5.3
Carbon dioxide, cc.	0.0	0.0	0.0	0.3	4.9
9.3 per cent methane in the gas mixture					
ETHANE					
Analysis	1	2	3	4	
Heater temp., ° C.	230	250	280	300	
Contraction, cc.	0.0	2.4	4.5	6.2	
Carbon dioxide, cc.	0.0	0.0	0.2	1.1	
3.4 per cent ethane in the gas mixture					
PROPANE					
Analysis	1	2	3	4	5
Heater temp., ° C.	130	150	180	220	400
Contraction, cc.	0.0	1.2	2.1	2.7	11.3
Carbon dioxide, cc.	0.0	0.2	0.2	0.7	5.4
21.7 per cent propane in the gas mixture					
BUTANE					
Analysis	1	2	3	4	
Heater temp., ° C.	120	140	160	400	
Contraction, cc.	0.0	1.5	2.8	12.9	
Carbon dioxide, cc.	0.0	0.9	1.1	7.1	
9.0 per cent butane in the gas mixture					

OXIDATION OF CARBON MONOXIDE IN CITY GAS

Although ethane begins to oxidize at 250° C., the rate of oxidation of the small amount present in city gas might be so slow as not to affect the results when hydrogen and carbon monoxide are oxidized together over the catalyst. The residues from three samples of city gas, containing carbon monoxide, hydrogen, methane, ethane, and nitrogen, were used to determine this. One analysis was run in which the carbon monoxide was determined by absorption in acid cuprous chloride, and hydrogen by oxidation in the catalyst tube at 100°. Other analyses were run in which both carbon monoxide and hydrogen were oxidized in the catalyst tube at 250° and at 300° C. The results are shown in Table II.

TABLE II. OXIDATION OF CARBON MONOXIDE AND HYDROGEN IN THE CATALYST TUBE

	Carbon Monoxide by Absorption	Carbon Monoxide by Catalyst Tube	
Analysis	1	2	3
Heater temp., ° C.	100	250	300
Number of passes	5	6	6
Hydrogen, per cent	32.3	36.8	36.9
Carbon monoxide, per cent	14.4	6.3	14.6

These results show that the oxidation of the ethane present in city gas is sufficient to affect the results for hydrogen. The rate of oxidation of the carbon monoxide at 250° C. is so slow as to preclude using this or a lower temperature at which ethane is not oxidized.

OXIDATION OF HYDROCARBONS OVER COPPER OXIDE

The copper oxide method was extensively used with no knowledge of the oxidation of hydrocarbons other than methane, until the recent work of King and Edgcombe (*2*), who studied the oxidation of methane, ethane, propane, and butane over copper oxide. They found that ethane, propane, and butane were slowly oxidized at 280° C., the temperature used for the determination of hydrogen and carbon monoxide. When the hydrocarbon was circulated over the copper oxide at 280° C. for 10 minutes in the Bone and Wheeler gas analysis apparatus, the following amounts of oxidation were found to have taken place: methane, 0.0; ethane, 0.8; propane, 1.0; butane, 1.4 per cent by volume. Various gas mixtures were also oxidized over copper oxide to study the effect of the oxidation of hydrogen and carbon monoxide on the oxidation of the hydrocarbons. The results are shown in Table III.

TABLE III. OXIDATION OF PARAFFIN HYDROCARBONS

(Oxidized over copper oxide at 280° C. in presence of hydrogen and/or carbon monoxide)

Composition of Gas Mixture						Analysis by Combustion		Paraffin Hydrocarbons Oxidized	
CH_4	C_2H_6	C_3H_8	CO	H_2	N_2	CO_2 formed	H_2	Mixture	Hydrocarbons
								%	%
..	31.0	..	16.8	51.6	0.6	17.3	51.1	0.25	0.8
..	..	29.7	..	69.8	0.5	0.7	69.2	0.23	0.8
..	..	25.8	14.0	59.8	0.4	14.5	59.3	0.17	0.7
34.0	64.0	..	..	..	2.0	1.0	..	0.5	0.8

King and Edgcombe conclude that with city gas, which does not normally contain more than 5 per cent of ethane, the amount of oxidation of ethane and higher homologs does not cause an error greater than that of measurement. However, with gases containing higher hydrocarbons, such as the gases from the low-temperature carbonization or hydrogenation of coal, errors due to oxidation of hydrocarbons may appreciably affect the accuracy of the analysis. Although King and Edgcombe found no oxidation of methane at 280° C., Campbell and Gray (*1*) state that the temperature should not exceed 300°. This is in contrast to the catalyst tube method where no oxidation of hydrocarbon takes place under the conditions for oxidation of hydrogen.

In studying the oxidation of hydrogen and carbon monoxide, King and Edgcombe found that if the carbon monoxide/hydrogen ratio exceeded 0.22, carbon monoxide would remain after all the hydrogen had been oxidized. As no volume decrease occurs when carbon monoxide is oxidized by copper oxide, the analyst must use precautions to insure its complete oxidation. The catalytic oxidation of carbon monoxide gives a volume decrease, so that complete oxidation may easily be attained.

ADSORPTION OF GASES

The adsorption of carbon dioxide by copper oxide introduces an error into the method of oxidizing carbon monoxide over copper oxide. Scherb (*6*) states that this occurs at room temperature, decreases with rising temperature, and becomes negative through dissociation at a red heat. King and Edgcombe (*1*) found appreciable disappearance of carbon dioxide when carbon monoxide is oxidized at 280° C. In order to recover all carbon dioxide they found it necessary to evacuate the reaction tube.

The adsorption of carbon dioxide over clear and platinized silica gels was studied by Reyerson and Swearingen (*5*) for pressure of carbon dioxide of about 740 mm. At 138° no carbon dioxide remained on the platinized gel; 1.78 cc. per gram remained on the clear gel, but this volume became zero at 218°. The platinized gel used by these workers contained much more platinum than the commercial platinized gel, though the adsorptive capacity of the latter is considerably less than that of the clear gel. Thus hydrogen and carbon monoxide can be determined together at 300° C. with no adsorption of carbon dioxide. This was also shown by the experiments reported in the first paper of this series (*3*).

Nothing has been reported concerning the adsorption of hydrocarbons by copper oxide. The adsorption of methane on silica gel was investigated by Reyerson and Swearingen (*5*) who found 1.35 cc. per gram at 0° and 740 mm. The small amount adsorbed at this low temperature indicates that no adsorption would occur at 100°. The adsorption of butane was investigated by Patrick and Long (*4*). At 100° they found 1.87 cc. per gram at 145.4 mm., 3.44 cc. per gram at 294.7 mm., 6.16 cc. per gram at 566.9 mm., and 7.45 cc. per gram at 696.5 mm. No data are available concerning the adsorption of ethane and propane. From the small amounts (low partial pressures) of ethane and higher hydro-

carbons present in city gas it may be concluded that adsorption will not be enough to affect the results. With gases containing greater amounts of the higher hydrocarbons adsorption will remove an appreciable volume from the gas mixture. However, a similar decrease in volume is caused by solution in fresh liquid reagents the first time the gas is bubbled through. After the liquid has become saturated with the gases no further volume decrease is due to this cause. The same thing is true of adsorption of gases on the catalyst. Since this adsorption is nonspecific (dependent only on the partial pressure of the gas) the catalyst will adsorb and come into equilibrium with the hydrocarbon mixture, so that no adsorption will occur in the second sample. The catalyst tube may be considered as introducing no more error than the liquid reagents used.

Conclusions

1. The oxidation of methane, ethane, propane, and butane over a commercial platinized silica gel has been studied. No oxidation occurs with methane at 350°, ethane at 230°, propane at 130°, or butane at 120° C., but oxidation does occur at temperatures 20° to 25° higher. Complete oxidation does not occur even at 400° C.

2. Hydrogen and carbon monoxide can be oxidized simultaneously at 300° C. in the presence of methane, but not when higher hydrocarbons are present, as in city gas.

3. A comparison of the copper oxide and catalyst tube methods has been made considering oxidation of higher hydrocarbons and adsorption of gases.

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Volume of Sugar-Beet Marc and Its Adsorptive Effect

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This paper is a continuation of work to establish the volume allowance for marc in the determination of sugar in beets by hot-water digestion. Fifty-eight determinations on thirty samples of cossettes by the Brown centrifugation method gave an average value of 1.0 ml. per 26 grams of cossettes for the volume of the marc, inclusive of the lead precipitate. No difference was found in the marc volume with the use of 6, 7, or 8 ml. of lead subacetate per 26 grams of cossettes. Tests made to determine the adsorption of water by marc from sugar solutions indicated that this effect, if any, is small under the conditions of the hot-water digestion, but may be sufficient to justify a somewhat higher marc allowance, the absolute value of which it is difficult to determine with precision by polarimetric methods.

The volume allowance for marc in digestion methods for determining sugar in beets has recently received renewed attention on the part of a number of investigators. In a previous paper Osborn and Brown (*3*) described the centrifugation method for this purpose, which is free from many of the drawbacks of other methods, and reported some preliminary determinations made on three samples of cossettes, which indicated a value of 1.0 ml. for the volume of the marc and lead precipitate in the normal weight (26 grams) of cossettes under the conditions of the hot-water digestion method. As the literature has been extensively reviewed by other authors (*3, 7, 8*), mention will be made here only of a few recent references.

Saillard (*5*) determined the weight and specific gravity of the washed and dried marc from 3 samples of rasped beets, finding a value equivalent to 0.9 ml. of marc, inclusive of the lead precipitate, per 26 grams of beets. In a communication (*6*) to the International Commission for Uniform Methods of Sugar Analysis Saillard stated the value as 1.2 to 1.3 ml. for the French double normal weight (32.52 grams), which is equivalent to 1.0 ml. per 26 grams. In the same communication he referred to some work done at the Kief Institute, in which the marc volume was calculated from the comparative polarizations obtained by digestion and by aqueous extraction. The average volume, in this case also inclusive of the lead precipitate, was 0.70 ml. per 26 grams of beets.

Spengler and Paar (*7*) have reported a number of tests in which the percentage of marc was calculated from the polarizations of sugar solutions made to volume with and without the presence of the normal amount of marc. In the presence of lead subacetate they found an average value of 0.83 ml. per 26 grams in the experiments made with pressed juice, and a little higher value with the use of pure sugar solutions. This value is not considered to include the lead precipitate, for which about 0.25 ml. should be added according to the author's data (*2*), and with this correction the volume would be 1.08 ml. Spengler and Paar also found marc volumes of about 1.5 to 2.5 ml. in the absence of lead subacetate, from which they conclude that beet marc contains considerable colloid water which is largely eliminated by the effect of the lead reagent.

Determinations by Centrifugation Method

During the 1932–33 campaign 58 determinations were made on 30 samples of ground cossettes from northern Colorado beets by the Brown centrifugation method (*3*). The procedure was as follows:

A hot-water digestion was made in the usual manner, except that half proportions were employed on account of the necessity of using 100-ml. flasks in the centrifuge. The 0.5 *N* weight (13 grams) of ground cossettes was rinsed into a 100-ml. flask with 3 to 4 ml. of lead subacetate (55° Brix.) and water to make

a volume of about 75 ml. After thorough deäeration under vacuum to remove air, the contents were digested 30 minutes in a water bath at 80° C., the flask was then filled slightly above the mark with hot water, and the digestion was continued 10 minutes longer.

After cooling, making to volume at 20° C., and mixing, the flask was weighed and then centrifugalized. As much of the clear supernatant liquid as possible (usually about 70 ml.) was drawn off carefully by suction into a test tube serving as a receiver, care being taken to avoid the loss of particles of the pulp or precipitate. The specific gravity of the clear liquid was determined in a pycnometer. The weight of "pulp" remaining in the flask was determined, and the entire amount of pulp was then dried in the flask to determine its moisture content. In this operation the excess of water was first evaporated off on a water bath, and the flask was then heated at 80° C. at an absolute pressure of 175 mm. of mercury in a vacuum oven, about 18 hours being required to attain constant weight. During the drying a slow current of air was aspirated through a tube extending almost to the bottom of the flask, to facilitate the removal of vapor. From the weights and analytical data the volume of the marc and lead precipitate was then calculated as described in the previous paper (*3*).

An International Equipment Company Type C centrifuge was used with a carrier and trunnion cups suitable for two 100-ml. flasks. The radius measured to the middle of the globular part of the flask was about 6.25 inches. In tests 1 to 21 the centrifuge was operated at a speed of 1100 to 1200 revolutions per minute, in subsequent tests at 1800 revolutions. The latter speed was preferable and gave a good separation in 10 minutes. A speed of 2900 revolutions was also tried, but was abandoned because of the difficulty of finding flasks that would not collapse at this speed.

Table I. Marc Volume

(With use of 6 ml. of lead subacetate per 26 grams of cossettes)

Expt.	Sugar	Marc per 26 Grams of Cossettes I	II	III	Av.
	%	*Ml.*	*Ml.*	*Ml.*	*Ml.*
1	15.3	1.10	..	..	1.10
2	14.5	1.06	..	..	1.06
3	17.0	0.98	0.96	..	0.97
4	16.3	0.84	1.06	..	0.95
5	16.0	1.10	..	..	1.10
6	15.3	0.83	0.92	..	0.88
7	16.0	0.85	0.91	..	0.88
8	17.1	1.00	0.91	..	0.96
9	17.6	1.05	1.06	..	1.06
18	16.0	0.77	0.91	..	0.84
20	14.8	0.87	..	..	0.87
21	16.9	0.99	1.00	..	1.00
24	16.3	0.93	..	..	0.93
25	14.2	0.83	0.96	0.93	0.91
26	14.5	0.92	0.91	..	0.92
31	16.3	0.98	..	..	0.98
Av.	15.9	..	..	..	0.96

Table II. Marc Volume

(With use of 7 ml. of lead subacetate per 26 grams of cossettes)

Expt.	Sugar	Marc per 26 Grams of Cossettes I	II	Av.
	%	*Ml.*	*Ml.*	*Ml.*
11	17.1	0.93	0.95	0.94
12	17.0	0.94	0.94	0.94
13	14.2	0.90	0.88	0.89
14	14.4	1.01	0.92	0.96
20	14.8	0.99	..	0.99
28	16.0	0.93	0.94	0.94
29	16.1	1.06	1.10	1.08
30	15.4	1.03	0.97	1.00
31	16.3	1.04	..	1.04
Av.	15.7	..	..	0.98

The marc values found, which also include the lead precipitate, are given in detail in Tables I to IV. The agreement between duplicates was satisfactory with a very few exceptions, being less than 0.1 ml. in most cases. No determinable difference was found with lead addition varying from 6 to 8 ml. per normal weight of cossettes. The minimum amount was apparently sufficient for clarification and the use of a larger quantity did not increase the amount of lead precipitate. In Table IV, in which four different lead additions were used on the same cossette samples, no difference is definitely established within the range of experimental error.

The average of all determinations and of each series, expressed to the nearest single decimal place, gives a value of 1.0 ml. for the volume of marc and lead precipitate per 26 grams of beets. This agrees well with the author's former values (*2*, *3*) and with the recent determinations by other methods of Saillard (*5*, *6*), and of Spengler and Paar (*7*) when the latter are corrected to include the volume of the lead precipitate. The value of about 1.5 ml. of Stanek and Vondrak (*9*) is distinctly higher.

Table III. Marc Volume

(With use of 8 ml. of lead subacetate per 26 grams of cossettes)

Expt.	Sugar	Marc per 26 Grams of Cossettes I	II	Av.
	%	*Ml.*	*Ml.*	*Ml.*
15	13.8	0.90	0.92	0.91
16	15.4	1.01	0.94	0.98
17	14.5	0.95	0.92	0.94
19	17.4	1.00	0.97	0.98
20	14.8	0.93	..	0.93
22	16.7	0.92	..	0.92
23	16.2	0.98	1.02	1.00
27	15.8	1.08	1.01	1.04
31	16.3	1.03	..	1.03
Av.	15.7	..	..	0.97

Table IV. Marc Volume

(With use of various amounts of lead subacetate)

Expt.	Lead subacetate, ml.:	Marc per 26 Grams of Cossettes 5	6	7	8
		Ml.	*Ml.*	*Ml.*	*Ml.*
20		0.78	0.87	0.99	0.93
31		1.07	0.98	1.04	1.03

An effort to plot the marc values against percentage of sugar has indicated a tendency to slightly higher marc volume with increasing sugar percentage, but this is so slight that it cannot be regarded as definitely established by the tests here reported.

Adsorptive Effect of Marc

It was claimed by early investigators that beet marc selectively adsorbs water from a sugar solution, with consequent increase in volume. The water thus loosely held was variously designated as water of imbibition, water of hydration, and colloid water. A good review of this early work is given by Rümpler (*4*). Vondrak (*10*) objected to the centrifugation method of determining marc volume because it does not take account of possible sorption of water by the marc in contact with the sugar solution. Mintz, Kartashov, and Trofimovskii (*1*) claim that the marc and lead precipitate adsorb sugar, although this view does not seem to be held by others.

The question has been confused by the fact that the method of preparation of the marc used by different investigators has varied. Under the conditions of the hot-water digestion method, the marc is heated to 80° C. for 30 or 40 minutes in the presence of lead subacetate. The temperature is probably not of great influence on the character of the marc because the cold-water digestion method is a standard method for the determination of sugar in beets which, with properly rasped pulp, is recognized as giving accurate results. The work of Spengler and Paar (*7*) is illuminating, however, in showing that the presence of lead subacetate largely nullifies the water-adsorptive capacity of the marc.

In order to obtain some information on the adsorptive effect of beet marc applicable to the conditions of the hot-water digestion method, several hundred grams of the marc and lead precipitate from hot water digestions were prepared by filtering, washing free of sugar, and air-drying at about 45° C. For convenience this material will be hereafter referred to simply as "marc." The effect on the polarization of sugar solutions was then determined independently by two analysts. A summary of the results is given in Table V.

Table V. Effect of Marc on Polarization of Sugar Solutions

Series	Description of Marc Used	Temp. of Digestion[a] ° C.	Analyst A: No. of tests	Analyst A: Control series	Analyst A: Marc series	Analyst A: Difference	Analyst B: No. of tests	Analyst B: Control series	Analyst B: Marc series	Analyst B: Difference
1	1 gram, air-dried	Cold	4	15.36	15.37	0.01	9	15.22	15.24	0.02
2	1 gram, dried at 80°	Cold	10	15.38	15.39	0.01	9	15.23	15.23	0.00
3	1 gram, dried at 105°	Cold	10	15.38	15.41	0.03	9	15.30	15.29	−0.01
4	1 gram, dried at 80°	80	10	15.38	15.39	0.01	6	15.29	15.28	−0.01
5	1 gram, dried at 105°	80	10	15.18[b]	15.18[b]	0.00	3	15.28	15.30	0.02
6	1 gram, air-dried	80	6	13.04[b]	13.02[b]	0.02	..	...	...	....
		Av.	50	14.80	14.81	0.01	36	15.26	15.26	0.00
7	5 grams, dried at 80°	Cold	..	...	...	..	4	15.25	15.38	0.13
8	5 grams, air-dried	Cold	10	15.35	15.47	0.12	..	...	...	....
9	5 grams, air-dried	80	10	15.35	15.44	0.09	..	...	...	....

[a] Period of 40 minutes in all cases.
[b] Digestion juice used in these series, pure sugar solutions in all others.

Except in the two series in which digestion juice (filtrate from a hot-water digestion) was employed, the procedure was as follows:

Approximately 2 grams of high-grade sugar were weighed out, dissolved in water, and made up to 100 ml. in a volumetric flask. The marc was then added and after 40 minutes' standing in the cold, or after hot digestion, the solution was filtered and polarized. In the hot digestion tests the flask was weighed before and after digestion, and any water lost by evaporation was restored. In connection with every series an equal number of sugar solutions, to which no marc was added, was polarized to serve as controls.

As in all marc investigations by polarimetric methods, careful work and a large number of determinations are required to minimize accidental error. In order to eliminate personal bias in reading a number of solutions of approximately the same polarization, the weight of sugar taken was allowed to vary between 1.95 and 2.2 grams, and the readings were afterwards calculated to the equivalent polarization per 2 grams of sugar. Usually five determinations and the same number of controls were handled at one time, the work being repeated to form a series of 10 determinations. In each set of 5 polarizations the difference between the highest and lowest polarization was usually not essentially over 0.1° and was sometimes less. Careful temperature control was exercised in making to volume and in the polarizations, which were made in a 400-mm. tube.

Table VI. Determinations of Marc Volume by Addition of Marc to Sugar Solutions

(1 gram marc in 100 ml.)

Series	No. of Tests	Polarization: Control series	Polarization: Marc series	Polarization: Difference	Calculated Volume for 2 Grams of Marc
					Ml.
1	5	15.31	15.40	0.09	1.2
2	5	15.37	15.48	0.11	1.4
3	5	15.34	15.46	0.12	1.6
Av.	15	15.342	15.448	0.106	1.37

The amount of sugar was chosen to give a polariscope reading about equal to that of a cossette polarization. In most of the work the marc was added in the same proportion to sugar in which it is present in a regular hot-water digestion of 0.5 *N* concentration. As the combined marc and lead precipitate have a specific gravity of about 2.0 (*2*), the calculated amount for 1.0 ml. of marc is accordingly 2 grams per 200 ml., or 1 gram per 100 ml. of solution, the amount used in these experiments. The average combined weight of the marc and lead precipitate from the digestion of 26 grams of cossettes was also found to be exactly 2 grams by direct weighing.

The air-dried marc showed about 2 per cent loss of moisture when heated at 80° and 3 per cent when heated at 105° C. The amount of moisture present in the marc dried at lower temperatures was therefore of negligible influence on the results. Several tests made by both analysts by extracting 1 and 5 grams of the marc with water and making up to 100 ml. showed zero polarization in all cases.

In the determinations of analyst A all solutions were made to volume and polarized at 20° C. The average polarizations of the control series in which sugar solutions were used are close to the theoretical value of 15.38 for pure sucrose. In the determinations of analyst B, various temperatures were employed to approximate the prevailing room temperature, but the same temperature was of course always employed for the parallel determinations and controls of each series.

The averages of all the tests and of each series made with 1 gram of marc show no determinable effect on the polarization. As the marc came from hot-water digestions, in which it had been heated at 80° C. for 40 minutes in the presence of lead subacetate, it was not expected that the variations in the temperature at which the prepared marc was dried, or the use of cold *vs.* hot digestion, would be of significance on the results, and this proved to be the case.

The three series made with the use of 5 grams of marc indicate consistently an adsorption of water equivalent to a polarization increase of the order of magnitude of about 0.1 sugar degree. This is equivalent to a polarization of 0.02° for each gram of marc, an amount which could hardly be definitely determined within the range of experimental error by polarizations made with the use of 1 gram of marc.

Some tests were also made in which the volume of the marc and lead precipitate was calculated from polarizations obtained in the following manner:

One gram of marc which had been dried at 105° C. and 1.95 to 2.2 grams of sugar were transferred to a 100-ml. flask, water was added, and the flask was evacuated to remove the air present in the marc, and then the regular hot-water digestion procedure was carried out, the solution finally being made up to 100 ml. at 20°. From the average polarization of a series of tests of this kind and of a control series composed of an equal number of determinations in which no marc was added, the equivalent marc volume was computed.

The averages of three series of this kind, which are given in Table VI, show consistently a higher value than that of 1.0 ml. obtained by the centrifugation method. Unfortunately the accuracy of polariscopic observation is not sufficient to establish the desired value with precision, as is illustrated by the fact that the difference of 0.4 ml. between the calculated volumes of the first and third series is due to a variation of only 0.03° in the polarization differences of the two series. It is therefore well not to attach too great importance to the absolute accuracy of these calculated marc volumes.

The difference between the use of a marc volume of 1.0 ml. or of 1.4 ml., the average of Table VI, would be equivalent to only 0.03° in the polarization of a beet containing 16 per cent sugar, so that within these limits the marc volume is established closely enough for practical purposes.

Acknowledgment

The author's thanks are due to J. A. Bair and J. W. Dickey for their careful manipulative work in the determinations of marc volume by the centrifugation method; to J. T. Davis for the preparation of the air-dried marc used in the adsorp-

tion tests; and to V. V. Hartman and C. A. Horne for their painstaking polarization work in the large number of tests made by them to determine the adsorptive effect of marc.

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Comparison of Extraction Formulas

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The process of extraction is frequently used for the removal of a desired compound from an impure solution of it. Thus the separation of an organic compound from an inorganic substance may usually be effected by extracting the aqueous solution with an organic solvent. A well-known general principle for the process is that, with a given quantity of extracting liquid, the use of many fractions of the liquid leads to a more nearly complete removal of the desired compound than does the use of the entire liquid in a single extraction. Formula 1 (*1*)

$$X_n = X_0 \left[\frac{KW}{KW + L}\right]^n \qquad (1)$$

where W = cc. of solution
X_0 = grams of substance dissolved therein
L = cc. of extracting solvent used in each extraction
K = distribution ratio of the substance for the two solvents
X_n = grams of substance remaining unextracted after the nth extraction

may be used to demonstrate the above principle and to compute the amount of substance which may be expected after a given number of operations.

As n is increased in the above formula X_n, the amount of substance remaining unextracted, will diminish and approach zero as a limit (X_0, K, W, L, and n being positive). Sometimes numerical examples are used to demonstrate this, but that the conclusion is valid in general is obvious, for from Equation 1 we may say

$$\frac{X_n}{X_0} = \frac{1}{(1 + L/KW)^n}$$

and putting $L/KW = \alpha$ we know that for positive values of α

$$(1 + \alpha)^n = 1 + n\alpha + \ldots \text{ positive terms}$$

becomes infinite as $n \longrightarrow +\infty$. Therefore $\frac{1}{(1 + \alpha)^n}$ and its equal $\frac{X_n}{X_0}$ must, as $n \longrightarrow +\infty$, approach zero as a limit.

The above case should be clearly distinguished from that in which the quantity of extracting liquid is not unlimited, as is always true in practice. While in this case, too, subdivision of the available liquid into many portions is advantageous, the limit of the process is not zero. If, in such a case, we consider L cc. as the total volume of extracting liquid and that it is to be subdivided into n equal parts, and these successively used, the formula obviously should be written

$$X_n = X_0 \left[\frac{KW}{KW + L/n}\right]^n = f(n) \qquad (2)$$

where, as before, X_0, K, W, L, and n are positive. (In the following differentiation, note that L is now a constant.) Proceeding on the basis that if the first derivative is negative the function is decreasing we seek to establish that

$$X_{n+1} < X_n \text{ or that } f'(n) < 0$$

$$f'(n) = X_0 \left[\frac{KW}{KW + L/n}\right]^n \left\{\frac{L}{n(KW + L/n)} + \ln\left[\frac{KW}{KW + L/n}\right]\right\}$$

Since the first term in the above equation is positive it is sufficient to study the sign of the remainder of the expression, i. e., that in braces.

Let us make the change of variable

$$L/KWn = u \quad \text{so that} \quad \lim_{n \to +\infty} u = 0$$

The first term (in braces) becomes $\frac{u}{1 + u}$ and the second $-\ln(1 + u)$, so that we study the sign of

$$\psi(u) = \frac{u}{1 + u} - \ln(1 + u) \text{ as } u \longrightarrow 0 \text{ by positive values}$$

Now $\psi(0) = 0$

(In general it may not be a fact that when the derivative is negative the function is negative. Here, however, the function is zero for u zero, and since its derivative is negative for u positive, it follows that the function is negative for u positive.)

$$\psi'(u) = \frac{-u}{(1 + u)^2}$$

Therefore $\psi(u) < 0$ for $u > 0$. Hence the function $\psi(u)$ has a graph below the axis of u for $u > 0$.

Thus also $f'(n) < 0$ and in particular

$$f(n + 1) = X_{n+1} < f(n) = X_n$$

or

$$X_{n+1} < X_n$$

Whereas X_n in Equation 1 approaches zero as n increases towards plus infinity, such is not true of X_n of Equation 2. In the latter case X_n obviously cannot approach the limit zero since in this case the total quantity of liquid, L, is finite. We evaluate this limiting constant as follows:

Starting with Equation 2 we may write

$$\ln \frac{X_n}{x_0} = \frac{\ln\left[\frac{KW}{KW + L/n}\right]}{1/n}$$

which takes the form 0/0 as $n \longrightarrow +\infty$. Therefore, differentiating both numerator and denominator

$$\lim_{n \to +\infty} \ln \frac{X_n}{X_0} = \lim_{n \to +\infty} \left[\frac{-L}{KW + L/n}\right]$$

Thus $$\lim_{n \to +\infty} \ln \frac{X_n}{X_0} = \frac{-L}{KW}$$

and $$\lim_{n \to +\infty} \frac{X_n}{X_0} = e^{-L/KW}$$

The limiting value, $e^{-L/KW}$, may also be established thus:

$$\lim_{n \to +\infty} \left[\frac{KW}{KW + L/n}\right]^n = \lim_{n \to +\infty} \left[1 + \frac{L}{KWn}\right]^{-n}$$

$$= \lim_{n \to +\infty} \left[(1 + L/KWn)^{KWn/L}\right]^{-L/KW} = e^{-L/KW}$$

However, the former method is necessary in order to show that $f(n)$ continuously—i. e., steadily or monotonically—decreases to its limiting value.

Summary

Two formulas used in the process of extraction are compared as concerns variables involved, especially with reference to the limits of extraction with an infinite and with a finite quantity of extracting liquid. These limits have been evaluated.

Acknowledgment

The writer is indebted to W. T. Read, W. E. Byrne, and H. S. White for criticizing the manuscript.

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Determination of Small Quantities of Nitrobenzene in Oils

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Occasions arise in which it becomes necessary to determine small amounts of nitrobenzene in petroleum oils. An outstanding instance is the process (*4*) for the refining of lubricating oils by extraction with nitrobenzene, where both the refined oil and the extract must be freed from small amounts of residual nitrobenzene. A comparative study of various methods has been made, selecting as the most promising the reduction with standard solutions of titanous salts and back-titration with ferric alum.

It was felt that the known difficulties of nitrogen determinations by combustion in a furnace or by a Kjeldahl procedure would be accentuated in the case of heavy oils. Another major line of approach lay in the reduction of nitrobenzene to aniline. Two variants of this would be (*a*) reduction with an excess of reducing agent followed by the determination of the excess, or (*b*) reduction followed by the determination of aniline. Under procedure *b* one might consider diazotization, colorimetric methods, or bromometric methods. Actual tests, however, showed that side reactions take place with nitrous acid, bromine, or similar reagents on account of the oil present, as was expected. The color of the oils precluded any hope of success by colorimetric methods. Variant *a* therefore was chosen. Under that head stannous chloride, titanous chloride, and titanous sulfate were chosen for consideration as reducing agents less likely to be affected by anything that may be present in the oils.

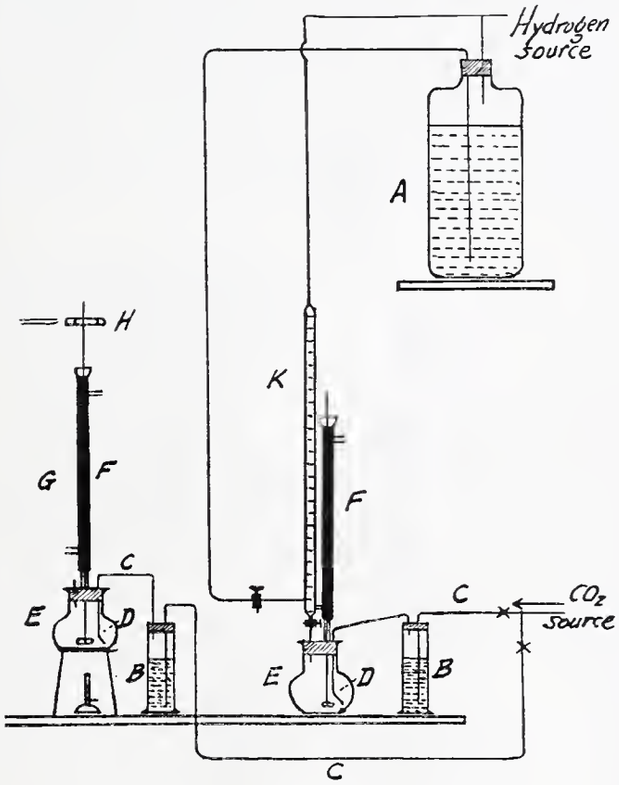

Figure 1. Assembled Apparatus

A. Titanous sulfate storage
B. Carbon dioxide wash tower with spiral
C. Carbon dioxide lines
D. Carbon dioxide inlet
E. Boiling flask
F. Condenser
G. Set-up in boiling position
H. Turbine
K. Titanous sulfate buret

Titanous chloride was soon ruled out on account of the formation of chloramines (*2*). A comparison of the action of stannous chloride (*5*) and titanous sulfate with reflux (*1*) showed superiority of the latter. Using known solutions of pure nitrobenzene the authors have been able to obtain 98 per cent reduction with 20 per cent excess titanous solution, whereas even 150 per cent excess stannous chloride gives only 80 per cent reduction. The reduction with stannous chloride is much slower as well.

Figures 1, 2, and 3 represent the apparatus developed for this determination.

Procedure

The procedure finally developed is as follows:

A sample of oil not exceeding 5 grams is weighed in the boiler, and 10 cc. of xylene, 25 cc. of methanol, and 25 cc. of 40 per cent sulfuric acid are

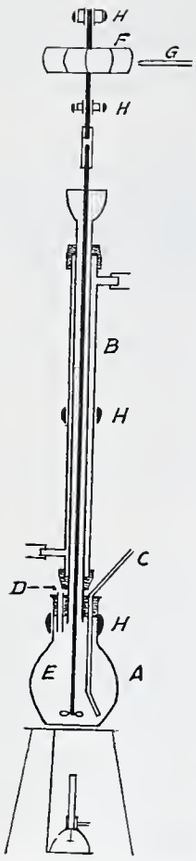

FIGURE 2. DIAGRAM OF APPARATUS

A. Boiling flask
B. Condenser
C. Carbon dioxide inlet
D. Hole for buret
E. Propeller
F. Turbine
G. Air jet
H. Clamps

added. The stopper containing the condenser, stirring rod, etc., is placed in the flask and carbon dioxide is bubbled through for 5 minutes. The flask is attached to the buret containing the reducing solution. The titanous sulfate is added in such a quantity that there will be a large excess present after the reduction. The flask is removed from the buret, the hole is plugged with the glass rod, and the stirrer is connected to the motor and the water circuit to the condenser. The mixture is gently boiled for 10 to 20 minutes with constant agitation. After heating it is cooled with cracked ice (to save time) and when cool is titrated with the ferric alum solution. When the blue of the titanous sulfate is almost completely removed, 10 cc. of 10 per cent ammonium thiocyanate are added through the top of the condenser as the indicator, and the titration is continued to the appearance of a pink end point lasting at least one minute. Carbon dioxide is bubbled through the apparatus during the entire procedure.

In most cases the separation of the oil was found not to be necessary. In the authors' experience, however, black tar-like samples were encountered which did not give consistent results with some observers unless the oil was separated after the reduction. This was referred to as the interference of the color with that of the end point. For such observers the end point is easier to define when the oil is separated. The apparatus in Figure 3 is used, and the separation is made when the end point color persists for only 15 or 20 seconds.

STRENGTH OF STANDARD SOLUTIONS

TITANOUS SULFATE. The strength of the titanous solution should be at least 0.08 N and preferably greater (0.2 N). As indicated in Table I, analyses of nitrobenzene samples and of oil containing nitrobenzene give much better results with the solutions of the higher normalities. The lowest results are obtained with a 0.05 N solution. The effect is more noticeable as the concentration of nitrobenzene increases. This decreased amount of reduction still held for the 0.05 N solution in spite of the fact that the amount of titanous solution was considerably increased, as well as the time of contact. It is apparent that the increased dilution of the mixture with water, due to the use of larger volumes of dilute titanous solution to obtain approximately the same amount of salt for contact, had an inhibitory effect on the reaction. This confirms Sampey's (*5*) work with stannous chloride wherein he states that the presence of water is inhibitory. With regard to the strength of titanous chloride solutions used in reductions, English (*3*) states that even for more accurate results a 0.25 N solution may be used without increasing the time of analysis. The author's experience has confirmed this and for the best results over a wide range of nitrobenzene concentrations they found a 0.2 N solution to be effective.

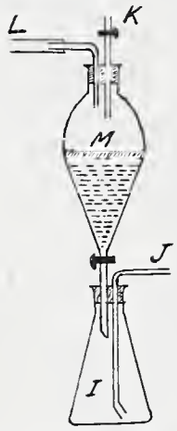

FIGURE 3. APPARATUS FOR SEPARATION OF OIL

I. Final titration flask
J. Carbon dioxide inlet
K. Outlet for carbon dioxide
L. Connection to *C*
M. Separatory funnel

TABLE I. NITROBENZENE IN OIL

Nitrobenzene (Approx.)	Titanous Sulfate	Nitrobenzene Present	Nitrobenzene Found	Deviation[a]
%	N	*Gram*	*Gram*	
0.01	0.20	0.0005	0.007	±0.0005
0.025	0.08	0.0013	0.0013	±0.0001
0.05	0.05	0.0021	0.0022	±0.0001
0.05	0.08	0.0020	0.0021	±0.0001
0.05	0.20	0.0023	0.0025	±0.0004
0.100	0.05	0.0036	0.0035	±0.0006
0.100	0.08	0.0049	0.0050	±0.0004
0.100	0.20	0.0057	0.0061	±0.0005
0.30	0.05	0.0137	0.0132	−0.0005
0.30	0.08	0.0127	0.0125	±0.0014
0.60	0.05	0.0240	0.0228	−0.0012
0.60	0.08	0.0198	0.0193	±0.0014
0.60	0.20	0.0245	0.0246	±0.0008
1.06	0.20	0.0191	0.0189	±0.0004
5.00	0.20	0.0300	0.0300	±0.0004
25.00	0.20	0.0300	0.0302	±0.0004
95.00	0.20	0.0285	0.0285	±0.0005

[a] Av. of 3 or more analyses.

Redistilled and recrystallized nitrobenzene is recommended for standardization. Ferric alum solutions of known strength have likewise been used.

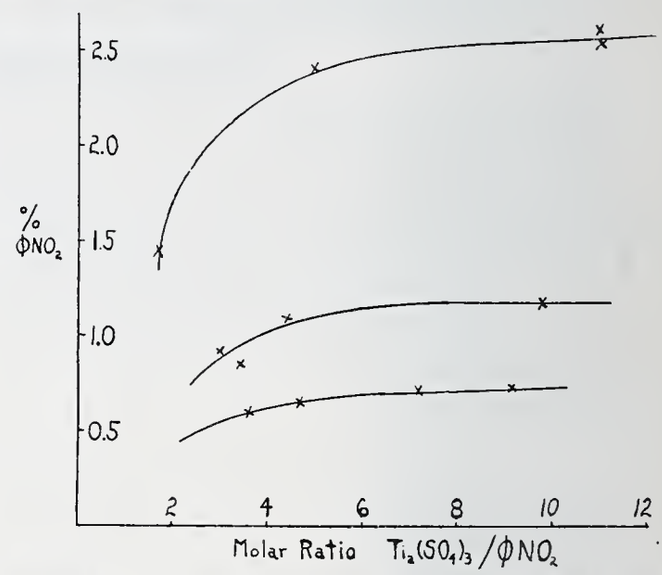

FIGURE 4. RATIO OF TITANOUS SULFATE TO NITROBENZENE

FERRIC ALUM SOLUTION. Ferric alum solutions varying from 0.02 N to 0.07 N have been used. For use with a 0.2 N titanous sulfate solution, the choice of a 0.05 N or 0.07 N ferric solution is made for obvious reasons.

RATIO OF TITANOUS SULFATE TO NITROBENZENE

In a reduction of this type wherein a large excess of the reducing agent is recommended, the question of limits arises. To clarify this point the authors have made a study of the significance of the ratio of moles of titanous sulfate to moles of nitrobenzene present in an analysis. This molar ratio has been proved to have a direct bearing on the reaction, which does not go to completion when the ratio is less than 10. In the early stages of the investigation molar ratios of 25 to 1 were used, but the results are not appreciably better than a 10 to 1 ratio. On the other hand, if a ratio of 5 is used the reduction will be less than 95 per cent complete, while for a ratio of 3 the reduction will be less than 80 per cent complete (Figure 4).

SIZE OF SAMPLE

For the sake of convenience and accuracy the size of the sample of oil is limited to not more than 5 grams. Table II

is presented as a guide, tabulating the convenient sized sample, with the volume of titanous sulfate solution required to give a molar ratio of at least 10 to 1.

Table II. Choice of Sample Size

Nitrobenzene Present	Sample Used	0.2 N $Ti_2(SO_4)_3$
%	*Grams*	*Cc.*
0.1	4	8
1	1.8	15
5	0.6	24
25	0.12	25
100	0.03	25

If the odor of nitrobenzene is pronounced, the sample will contain as a minimum approximately 0.1 per cent of nitrobenzene.

Discussion

The oil has no appreciable effect on the titanous sulfate. A number of samples of oil were selected as typical of those actually encountered in practice. The average variation was equivalent to 0.005 per cent (0.0002 gram from 5-gram sample) of nitrobenzene ±0.005 per cent, the variation tending largely in the negative direction. An average accuracy of 98 ± 10 per cent may be expected for concentrations of nitrobenzene from 0.025 to 0.65 per cent, when an 0.08 N solution is used and for higher concentrations of nitrobenzene greater accuracy is attained with a 0.2 N solution. The variations may seem large when considered from the standpoint of the per cent accuracy. On the other hand, if one considers the actual weights of nitrobenzene present and found as indicated in Table I, the values are indeed small. In the light of the authors' experience there is no doubt that a much higher degree of accuracy could be obtained by using a larger sample and a much stronger titanous solution, but the procedure would be entirely precluded from use as a control method, because of the expense of the titanous sulfate.

For further details on technic one is referred to English's work (*3*). Other provisions made involved the treating of the rubber stoppers with boiling sodium hydroxide and dilute sulfuric acid and the use of a sodium carbonate solution containing pyrogallic acid for scrubbing the carbon dioxide.

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Separation of Gold from Tellurium

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Tellurium can be separated satisfactorily from gold by reduction of the auric ion to elementary gold by either nitrous acid or ferrous sulfate. By a combination of one of these methods and a slight modification of the Lenher-Homberger method for the determination of tellurium it is possible to determine both gold and tellurium in the presence of each other.

The common gravimetric methods used for the determination of gold and tellurium consist of reducing the gold or tellurium ion to the elementary state and weighing as the element. The separation of gold from tellurium may be accomplished if we have a system of sufficiently low potential to reduce gold but high enough not to reduce tellurium. Such reducing agents as sulfurous acid and hydrazine will reduce both gold and tellurium. Hutchins (*2*) found that nitrous acid would not reduce either telluric or tellurous acids, but Fisher (*1*) has shown that nitrous acid quantitatively reduces gold from its solutions. During the course of the present investigation it has also been found that gold may be reduced from its solutions in the presence of tellurium by ferrous sulfate. This investigation was undertaken to establish the conditions under which gold might be separated quantitatively from tellurium by reduction with nitrous acid and with ferrous sulfate.

Materials

Solutions of gold chloride were prepared by dissolving gold in aqua regia, evaporating to dryness, and diluting with water. These solutions were standardized, taking aliquot portions and reducing with an aqueous solution of sulfur dioxide. Solutions of tellurium chloride were prepared by dissolving pure tellurium dioxide in concentrated hydrochloric acid and diluting with water. The hydrogen chloride content of the solutions of tellurium was adjusted to approximately 12 per cent (3.3 M). The tellurium solutions were analyzed according to the method of Lenher and Homberger (*3*).

Precipitation of Gold with Nitrous Acid

When a solution of auric chloride is reduced with sodium nitrite the quantity of gold precipitated is a function of the hydrochloric acid content of the solution and probably more specifically of the pH of the solution. If the pH is less than 1 the gold is not precipitated quantitatively and at a pH of 0.67 the error is about 3 per cent.

Since it is necessary to have hydrochloric acid in solution in order to prevent the hydrolysis of tellurium tetrachloride, the reduction should be carried out in the presence of a buffer salt. It was found that buffers which gave a solution whose pH was above 5 gave precipitates of gold which were so finely divided that they could not be quantitatively separated by filtration. For this reason borax and sodium acid phthalate were not satisfactory. There also is danger of hydrolysis of tellurium to hydrated tellurium dioxide at the higher pH. Sodium acetate as a buffer gave fairly satisfactory results.

To 20 ml. of gold chloride solution were added 50 ml. of a 10 per cent solution of sodium acetate and 5 ml. of constant-boiling hydrochloric acid. Then 25 ml. of a 4 per cent solution of sodium nitrite were added and the total volume was brought to about 150 ml. and heated to boiling. The gold was filtered onto a Gooch crucible and dried to constant weight at 110°. The pH of the filtrate was about 1.6. The error in a series of six determinations in which 0.1568 gram of gold was taken varied from one to three parts per thousand low, probably because of the loss of a small amount of precipitated metal through the asbestos mat of the Gooch.

Better results were obtained by using Rochelle salts, sodium potassium tartrate, as a buffer.

To 100 ml. of a solution of gold chloride were added 100 ml. of a 20 per cent solution of Rochelle salts, and 25 ml. of a 4 per cent solution of sodium nitrite, and the volume was adjusted to 250 to 275 ml. The solution was allowed to stand until the gold had settled and was then brought to boiling and the gold was filtered onto a tared Gooch crucible, washed, dried at 110°, and weighed. The filtrate from such a precipitation had the following pH when the respective amount of constant-boiling hydrochloric acid had been added: 1 ml., 2.4; 5 ml., 1.8; 10 ml., 1.5; 25 ml. 0.65. When the pH is less than 1 the gold is not quantitatively precipitated, but at a pH of 1 to 3 the error is from one to two parts per thousand low.

These results clearly indicate that Rochelle salts are a satisfactory buffer for use in the precipitation of gold with nitrous acid in the presence of a limited amount of hydrochloric acid.

Precipitation of Gold with Ferrous Sulfate

Although the precipitation of gold with ferrous sulfate is frequently referred to, textbooks and the literature do not give details which are essential for the success of an analysis by this method. The following procedure was found to give satisfactory results:

A solution of gold chloride containing a known amount of gold was taken and to this were added 10 to 12 ml. of concentrated hydrochloric acid and sufficient distilled water to bring the total volume to about 175 ml. The solution was heated to boiling and 1.5 grams of ferrous sulfate were added. The solution was now boiled for 10 to 15 minutes or allowed to stand on the sand bath at 80° C. for 24 hours and the precipitated gold was filtered onto a tared Gooch crucible, washed, dried at 110°, and weighed.

In a series of six experiments, taking 0.0948 gram of gold in each, the error in gold found varied from −0.0002 to +0.0003 gram.

Separation of Gold from Tellurium with Nitrous Acid

An attempt was made to precipitate gold in the presence of tellurium, using sodium acetate as a buffer.

To 20 ml. of a solution of gold chloride and 10 ml. of tellurium tetrachloride were added 50 ml. of a 10 per cent solution of sodium acetate. This caused a hydrolysis of tellurium which resulted in the precipitation of hydrated tellurium dioxide, and it was necessary to add 2 to 3 ml. of concentrated hydrochloric acid in order to dissolve the tellurium. The solution was heated almost to boiling, and 25 ml. of a 4 per cent solution of sodium nitrite were added. The precipitated gold was filtered on a tared Gooch crucible, washed, dried at 110°, and weighed.

The pH of the filtrate from these precipitations was usually somewhat less than 1, and it was necessary to have a sufficient excess of hydrochloric acid to give this pH and thus prevent the hydrolysis of tellurium tetrachloride. The method is not applicable to the separation of gold from tellurium, since the errors were of the order of three to five parts per thousand low in a series of five determinations.

Table I. Separation of Gold from Tellurium by Precipitation with Nitrous Acid in the Presence of Rochelle Salts as Buffer

Gold Taken	Tellurium Taken	Gold Found	Error
Gram	*Gram*	*Gram*	*Gram*
0.1450	0.1283	0.1449	−0.0001
0.1450	0.1283	0.1451	+0.0001
0.1450	0.1283	0.1449	−0.0001
0.1941	0.5000	0.1940	−0.0001
0.1941	1.0000	0.1937	−0.0004
0.1941	1.0000	0.1941	0.0000

The use of Rochelle salts as a buffer proved more satisfactory, however. The method developed is as follows:

One hundred milliliters of a 20 per cent solution of Rochelle salts are added to the solution containing gold and tellurium, and then followed by 25 ml. of a solution of sodium nitrite. The volume of the solution should not exceed 275 to 300 ml. and the hydrochloric acid content must be below 1 to 1.5 per cent. After the gold has separated, the solution is brought to boiling and the gold is filtered and weighed. The results of a typical series of determinations are given in Table I.

Separation of Gold from Tellurium with Ferrous Sulfate

The following procedure was developed for the separation of gold from tellurium with ferrous sulfate:

To a solution containing gold and tellurium, sufficient hydrochloric acid was added to bring its concentration to 1.5 to 2 per cent hydrogen chloride. The total volume of the solution was adjusted to about 175 ml., heated to boiling, 1 to 1.5 grams of ferrous sulfate were added, and the solution was boiled for 10 to 15 minutes. The gold was filtered onto tared Gooch crucibles, dried and weighed or filtered onto filter paper, ignited, and weighed. The results are tabulated in Table II.

Table II. Separation of Gold from Tellurium by Precipitation with Ferrous Sulfate

Gold Taken	Tellurium Taken	Gold Found	Error
Gram	*Gram*	*Gram*	*Gram*
0.1084	0.1281	0.1083	−0.0001
0.1084	0.1281	0.1082	−0.0002
0.1084	0.1281	0.1084	0.0000
0.1084	0.1140	0.1082	−0.0002
0.1496	0.1140	0.1495	−0.0001
0.1496	0.1140	0.1497	+0.0001

Determination of Gold and Tellurium in Presence of Each Other

The simultaneous precipitation of gold and tellurium may be effected by following the method of Lenher and Homberger (*3*) with the modification of using double the volumes of reducing agents suggested by them.

Twenty millimeters of a solution containing gold and tellurium were taken and the concentration of hydrochloric acid was adjusted to 12 per cent (3.3 *M*). The solution was heated to boiling, and double the volumes of reagents (solutions of 15 per cent hydrazine hydrochloride and saturated solution of sulfur dioxide) were added as called for by Lenher and Homberger (*3*). The gold and tellurium were filtered, dried, and weighed. The precipitate was dissolved in aqua regia and evaporated several times with hydrochloric acid; the gold was separated as described above, using Rochelle salts and nitrous acid, and the weight of tellurium was obtained by difference. The results are tabulated in Table III.

Table III. Determination of Gold and Tellurium

Gold Taken	Tellurium Taken	Gold and Tellurium Found	Gold Found	Error	Tellurium Found	Error
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0760	0.0593	0.1351	0.0759	−0.0001	0.0592	−0.0001
0.0760	0.0593	0.1352	0.0758	−0.0002	0.0594	+0.0001
0.0760	0.0593	0.1351	0.0759	−0.0001	0.0592	−0.0001
0.0760	0.0593	0.1351	0.0759	−0.0001	0.0592	−0.0001
0.0760	0.0593	0.1352	0.0761	+0.0001	0.0591	−0.0002
0.0760	0.0593	0.1352	0.0760	0.0000	0.0592	−0.0001

Summary

Gold may be precipitated quantitatively in the presence of limited amounts of hydrochloric acid (about 1.5 per cent of hydrogen chloride, 0.45 *M*) with nitrous acid, using sodium potassium tartrate (Rochelle salts) as a buffer. The pH of the solution should be greater than 1, but in the higher pH region gold is precipitated in such a finely divided form that it cannot be filtered.

Gold may be precipitated quantitatively in the presence of hydrogen chloride (1 to 2 per cent) with ferrous sulfate.

Gold may be separated from tellurium by reduction with nitrous acid in a solution buffered with Rochelle salts and having a hydrogen chloride content of 1.5 per cent or less (0.45 *M*), or by reduction with ferrous sulfate in a solution having a hydrogen chloride content of 1 to 2 per cent (0.3 to 0.6 *M*).

Gold and tellurium may be determined in the presence of each other by first precipitating the gold and tellurium together and then separating the gold by reduction with nitrous acid.

ACKNOWLEDGMENT

The subject for this investigation was suggested in 1917 by the late Victor Lenher. The experimental work was started in Professor Lenher's laboratory at the University of Wisconsin in 1917, was continued with Professor Lenher's permission by D. C. Knowles in 1926–27, and part of this paper is based upon the thesis presented by Mr. Knowles in partial fulfilment of requirements for the degree of Bachelor of Science at the Polytechnic Institute of Brooklyn, in June, 1927. The authors are pleased to acknowledge their indebtedness to Douglas Fronmuller, who has made several series of determinations. Publication in the present form is with the permission of Samuel Lenher.

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Determination of Borate Ion in Ores of Borax

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IN 1932, Scott (*3*) published the results of research on the determination of boric acid in the ores and mill products so abundantly produced from the mines in Kern County, Calif., which at the present time are the only source of borax ore in the United States. He concluded with a formal method based upon the results of these researches. The death of Doctor Scott prevented further research along the original lines, but as one of the participants in these investigations, the present author has continued the work and now offers a completed analytical method differing from Scott's directions in some essential particulars.

In general it is the method originally proposed by Thomson in 1893 and presented in revised form in 1908 by Wherry (*5*). In so far as it relates to titrating boric acid it has been officially accepted by the Association of Official Agricultural Chemists and by the American Ceramic Society, and for routine work has been approved by Hillebrand and Lundell, of the U. S. Bureau of Standards. With more or less incomplete detail it has been copied by standard books on chemical analysis, and is merely elaborated here. It is offered as a procedure applicable to all borate ores, to partially refined products, and to completely crystallized borax. By a more drastic decomposition treatment it may be applied to the analysis of the borosilicate minerals and glasses (*4*).

Borate minerals—borate ores and mill products—need not be ground finer than 30 mesh. Finer grinding of many of the calcined products results in a loss of values by dusting. All milled material is hygroscopic, cannot be dried to any permanently constant weight, and samples should be kept in tightly stoppered containers. Close checks by different laboratories are practically impossible.

The method is based upon the precipitation of the bases of the iron-alumina group from an acid borate solution and titration of the liberated boric acid with sodium hydroxide. Wherry (*5*) used calcium carbonate in neutral or alkaline solution as the precipitant, reprecipitating two or three times and washing carefully. Sullivan and Taylor (*4*) did the same, but separation under these alkaline conditions was never quite satisfactory and Wherry says that the method is not to be recommended. Wherry also tried an acid separation but did not follow it up. Scott's researches included acid precipitation using phenolphthalein indicator as control, demonstrating in this way that no aluminate passed into the filtrate to interfere with the boric titration, but he did not include this plan in his final method. The author follows Scott's sodium hydroxide–acid separation but with a modified procedure which involves only one precipitation and avoids all error by occlusion.

PROCEDURE

To 2.5 grams of the suitably prepared sample in a 100-ml. tall plain covered beaker add 5 or 10 ml. of water to wet the mineral and then 10 ml., pipet measure, of 6 *N* hydrochloric acid (1 to 1). Digest for at least 30 minutes on top of the water bath, with occasional agitation but without removing the cover. All borate ores are thus readily decomposed without loss of boron or the use of an excessive amount of acid (*2*). Remove from the bath, wash down the cover and beaker with plenty of cold water, and filter into a 250-ml. graduated flask, washing the insoluble matter with hot water only. (Ignite and weigh the insoluble mineral matter if that item is desired.) It may be tested qualitatively for boron; but the author has never found any, and such insoluble borate would not be considered available boric acid.

To the filtrate, which will amount to about 200 ml., add carefully, preferably from a buret, a strong sodium hydroxide solution until the liquid is nearly neutralized, using methyl red as indicator. This condition is necessary for the removal of carbon dioxide by boiling. A precipitate of iron and aluminum hydroxides will appear just before neutrality is reached and if the liquid is still acid to methyl red a proper condition obtains for the removal of carbonate by boiling. Adapt an air-condenser tube to the flask, such as the inner tube of a 24-inch (60-cm.) Liebig condenser, and heat to gentle boiling for at least 15 minutes, allowing the steam to rise not higher than half way up the condenser. All carbon dioxide will be removed without loss of boron and the iron-alumina hydroxide precipitate will occlude no boric acid. Under these conditions methyl red in the presence of free boric acid shows an acid reaction at pH of 6, and both iron and aluminum hydroxides are precipitated. Borates do not form until a pH of about 11; hence the precipitates carry no boron.

Remove the flask from the heat, wash down the condenser with cold water, and cool the flask as rapidly as possible without undue exposure to the air. As soon as cool, add at once sufficient calcium hydroxide solution to fill the flask to the mark. This will make the solution alkaline without introducing any soluble carbonate and any residual iron or alumina will precipitate. Mix thoroughly and filter on a dry paper and into a dry beaker. Do not wash, but as quickly as possible pipet off two aliquots for the final titration.

TITRATION

Titrations should be conducted as quickly as possible after the aliquots are taken, using a standard hydroxide practically

free from carbonate. To each aliquot in a flask add methyl red and a drop of hydrochloric acid just sufficient to turn it red. Then from the titration buret add hydroxide until the methyl red just turns a full lemon-yellow. Do not stop at the so-called neutral tint. The solution will then be alkaline to hydrochloric acid, at a pH of about 10, and will be practically neutral to phenolphthalein and boric acid at about the same pH. The differences are well within the color indicator errors of titration. (Allen and Zies (*1*) working on borosilicate glass found a difference of 0.3 mg. B_2O_3 between the end point with *p*-nitrophenol and the beginning with phenolphthalein. The author has not been able to confirm this error using methyl red, although theoretically some alkali should be consumed.)

To this neutralized solution add an excess of mannite and titrate to a permanent red with phenolphthalein, a color which is not bleached by further addition of mannite. If sufficient mannite is added at the beginning, the solution will be nearly colorless until the final red. In absence of excess mannite a pink color will maintain during much of the titration and a true end point will be reached only when a single drop of the alkali gives a red that does not fade. Using 0.2 *N* alkali, titrations will habitually check to 0.1 cc. equivalent to 0.7 mg. of B_2O_3 or less than 0.1 per cent on 1 gram titrated.

Check analyses in this laboratory recently ran as follows: 38.80, 33.07, 29.67, 29.55, 44.61, 44.10, 41.01, 42.19, 42.07, 38.81, 33.22, 29.77, 29.62, 44.69, 44.25, 41.15, 42.19, 42.14, routine work. Two drops of 0.2 *N* alkali will always indicate an end point and the quantitative reaction between sodium hydroxide and boric acid in the presence of a polyhydric alcohol has never been brought into dispute.

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Determination of Iron

Adaptation of the Mercaptoacetic Acid Colorimetric Method to Milk and Blood

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THE mercaptoacetic acid colorimetric method of Lyons (*9*) for the determination of small quantities of iron offers advantages over the thiocyanate colorimetric method of Elvehjem (*3*) as adapted from Kennedy (*6*), in that smaller samples may be used, thus making wet-ashing practicable and avoiding the losses and contaminations encountered in the dry-ashing procedure, and in that the color produced is more stable.

The authors' experiments confirmed observations of Andreasch (*1*), Ginsburg and Bondzynski (*4*), and Claesson (*2*) on the formation of an intensely blue or purple compound by the reaction of mercaptoacetic acid (thioglycollic acid) with ferric chloride in ammoniacal solution, the tendency of the color to fade, and the ready restoration of the color when the solution is shaken with air.

Preliminary experiments with a standard iron solution (0.005 mg. of iron per cc.) showed that for quantities of iron between 0.0025 and 0.025 mg., the colored solutions could be conveniently compared in tubes of uniform diameter, such as Nessler tubes, and that it was not necessary to dilute to volume, as the addition of distilled water to the solutions in the tubes caused no noticeable change in color intensities of the columns when observed through their entire depths. For quantities of iron from 0.015 to 0.1 mg., dilution to volume and the use of the colorimeter are recommended. Larger quantities of iron necessitate dilution and the production of color in convenient aliquots.

Comparison of color-development by the use of 2 drops of undiluted mercaptoacetic acid, 1 cc. of a 1 to 15 aqueous solution of the acid, 1 cc. of a 1 to 15 alcoholic solution, and 1 cc. of a 1 to 15 aqueous solution rendered alkaline with ammonium hydroxide (the reagent described in the next section) favored the last as it combines the advantages of nearly eliminating the unpleasant odor of the mercaptoacetic acid with good control of the amount of reagent added.

Experiments on wet-ashing of milk with sulfuric acid, sulfuric and nitric acids (*8*, *10*), and sulfuric and perchloric acids (*5*, *7*) were performed. The ashing with sulfuric acid alone was too slow, and with nitric acid resulted in muddiness and other irregularities in the colors developed, whereas the colors with perchloric acid were like those developed when standard iron solutions were used.

Method

Reagents. Iron-free concentrated sulfuric acid, 60 per cent perchloric acid, concentrated ammonium hydroxide, standard iron solutions, and the mercaptoacetic acid reagent are necessary.

The standard iron solutions are prepared by dissolving 1 gram of pure iron wire in dilute sulfuric acid and oxidizing with concentrated nitric acid. The oxides of nitrogen and excess nitric acid are expelled by boiling. The solution is diluted to 1 liter, with further dilution as needed. In all dilutions it is advisable to add extra sulfuric acid to prevent hydrolysis of the dissolved iron salts to insoluble basic compounds.

The mercaptoacetic acid reagent is prepared by the addition of 4 cc. of mercaptoacetic acid to a solution of 8 cc. of concentrated ammonium hydroxide in 50 cc. of water.

Determination of Iron in Milk. Samples[1] of 5 cc. of milk (or 0.5 gram dried milk) are digested with 3 cc. of con-

[1] With samples of this size, there was rarely any turbidity from precipitation of alkaline earth phosphates in the final ammoniacal solution. Filtration of occasional turbid samples through small iron-free filter paper gave clear solutions with colors matching those of the duplicates which were not turbid. Filtration of very turbid solutions from larger samples gave entirely satisfactory results.

centrated sulfuric acid and 2 cc. of perchloric acid in micro-Kjeldahl flasks on an electric heater until colorless and the excess of perchloric acid has been driven off. The perchloric acid is added in 0.5-cc. portions, one after the sulfuric acid, the second to the cooled flask after the charring is quite decided, and the remaining portions if, and as, needed. The digestion requires from 30 minutes to 2 hours. When the digestion is complete, the contents of the flask are transferred to a 150-cc. beaker, the flask is rinsed two or three times with small volumes of distilled water, the liquid cooled, and the acidity adjusted by the addition of concentrated ammonium hydroxide from a dropping bottle until just alkaline to litmus (a very small piece of litmus paper may be kept in the solution), then made just acid with concentrated sulfuric acid and an excess of from 5 to 10 drops of acid added. One cubic centimeter of the mercaptoacetic acid reagent is added and the solution made strongly alkaline by the addition of 1 to 2 cc. of concentrated ammonium hydroxide. The colored solution thus formed is compared with a series of standards in narrow tubes (12 × 20 mm.); therefore the volume should be kept below 20 cc. If the volume is too large for these tubes, other tubes of uniform diameter and appropriate capacity, such as Nessler tubes, may be used.

Table I. Results of Iron Determinations by Mercaptoacetic Acid Method

Sample	Volume	Iron Added	Iron Found	Iron[a]
	Cc.	*Mg.*	*Mg.*	*Mg./-100 cc.*
Goat's milk A	5	...	0.0035, 0.0035	0.07
Goat's milk A	5	0.005	0.008+	0.06+
Goat's milk B	5	...	0.004−, 0.004−	0.08−
Goat's milk B	5	0.003	0.0065+	0.07+
Goat's milk C	5	...	0.003, 0.0035	0.065
Goat's milk C	5	0.003	0.006	0.06
Goat's milk D	5	...	0.0035, 0.003, 0.003	0.0063
Jersey cow's milk	5	...	0.0035, 0.004	0.075
Jersey cow's milk	5	0.003	0.0065	0.07
Milk from local market	5		0.0035	0.06
			0.003, 0.003−	
	Gram			
Dried milk	0.563	...	0.0058	1.03
Dried milk	0.507	...	0.0056	1.10
Dried milk	0.584	...	0.0058	0.995
Dried milk	0.577	...	0.0059	1.02
	Cc.			
Hog's blood[b]	0.02[c]	...	0.0100, 0.0104	51.0
Hog's blood[b]	0.01[c]	...	0.0050, 0.0053	52.3
			0.0053, 0.0052	...
			0.0054, 0.0052	...
			0.0052	...
Hog's blood[b]	0.02[d]	...	0.0100, 0.0103	...
			0.0104, 0.0104	52.8
Guinea pig's blood[b]	0.2[e]	...	0.080, 0.086, 0.080	41.0
Guinea pig's blood[b]	0.1[f]	...	0.045, 0.045, 0.045	45.0
Guinea pig's blood[b]	0.1[f]	0.02	0.06, 0.063	41.5

[a] The added iron was subtracted before the calculation of mg. per 100 and the results are for 100 cc. excepting in the case of dried milk where they are for 100 grams.
[b] See also section "Comparison with Other Methods."
[c] Measured with blood pipet.
[d] 2 cc. of 1 to 100 dilution.
[e] 2 cc. of 1 to 10 dilution.
[f] 1 cc. of 1 to 10 dilution.

The standards for color comparison are prepared by the substitution of 1 to 5 cc. of appropriate standard iron solutions for the sample to be analyzed. The entire procedure in the preparation of the colored standards must be identical with that for the sample.

The standards occasionally fade within an hour; however, the color is satisfactorily restored if the solution is then shaken with air. Standards are often satisfactorily revived even after they have been allowed to stand for 24 hours or more. It is, however, advisable to replace some of the members of the series of standards every day to verify the values of the older solutions.

Table I gives results obtained by the application of this procedure to goat's milk, cow's milk, and milk powder.

Determination of Iron in Blood. Samples of 0.01 or 0.02 cc. of blood are taken with the blood pipet, transferred with dilution to the micro-Kjeldahl flasks, and digested with 1 cc. each of concentrated sulfuric and perchloric acids. The remainder of the procedure is the same as described above.

Table I includes data for determinations on hog's blood by this procedure, and by using 1- and 2-cc. portions of a 1 to 100 dilution, and also data from some earlier experiments with guinea pig's blood in which amounts equivalent to 0.1 and 0.2 cc. were taken from a 1 to 10 dilution. In the latter case, the final volume of the colored solutions was 25 cc. and the colors were compared in the colorimeter.

Comparison with Other Methods. Kennedy's thiocyanate method applied to the sample of guinea pig's blood, ranging from 0.1 to 0.4 cc., with and without added iron, gave results which when calculated for 1-cc. samples are 0.42, 0.39, 0.40, 0.395, 0.435, and 0.414 mg., respectively. The average is 0.412 mg., compared with an average of 0.423 mg. for nine determinations by the mercaptoacetic acid method, which are given in the table.

Hog's blood was used for a macrodetermination of iron by the digestion of 25-cc. samples with 60 cc. of concentrated sulfuric acid, dilution, reduction of the ferric iron to ferrous by pure zinc, and titration with standard permanganate solution. The iron found was 13.375 and 13.350 mg., respectively. Calculated for 100-cc. samples, the average is 53.75 mg., compared with 52.0 mg. for the mercaptoacetic acid method (Table I).

Other Applications. This method was applied to eggs and to feces. Because of the larger quantities of iron the procedure for milk was modified as follows: two-gram samples were used, the product of digestion was diluted to 50 cc., and 10-cc. aliquots were used for color development without the adjustment of the acidity prior to the addition of the mercaptoacetic acid reagent. Either tubes or the colorimeter may be used.

Summary

The mercaptoacetic acid method for the determination of small amounts of iron has been adapted to the analysis of milk and blood.

Wet-ashing with sulfuric acid and perchloric acid has been found satisfactory and avoids the contaminations and losses encountered in the dry-ashing procedures.

Acknowledgment

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Japan to Manufacture Silicon Carbide. Large-scale production of silicon carbide is proposed by Japanese interests, according to the Department of Commerce. Last year Japan's imports of "mineral substance for grinding or polishing" amounted to 3120 metric tons, valued at 939,000 yen, of which the United States supplied approximately 50 per cent. Annual consumption of silicon carbide in Japan is approximately 1000 metric tons. Two Japanese companies have started production on a commercial basis, and it is expected that their combined output will materially reduce imports of artificial abrasives.

Direct Determination of Chromium and of Vanadium in Steel

o-Phenanthroline Ferrous Complex as Indicator

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After oxidizing chromium and vanadium in a steel by the perchloric acid method and adding a measured excess of ferrous sulfate to reduce the chromic and vanadic acids, the excess may be titrated at room temperature with standard permanganate, using o-phenanthroline ferrous complex as an oxidation-reduction indicator. The reaction between permanganate and vanadyl ions in this solution of high acidity is sufficiently slow so that an excellent end point is obtained. If the hydrogen-ion concentration of this solution is reduced and the temperature raised somewhat, the vanadyl ion may then be titrated with standard permanganate because the indicator has such a high oxidation potential that it is not affected by the vanadic acid formed in this reaction. This gives a rapid indicator method of determining both chromium and vanadium in a single sample.

The same double titration may be used after oxidation of the chromium and vanadium in a steel by the permanganate-azide or persulfate–hydrochloric acid method. Neither of these methods is as rapid as the perchloric acid method.

THE most exact methods at the present time for chromium involve the direct titration of the chromic acid, obtained from a persulfate or similar oxidation, with standard ferrous sulfate. The end point may be determined either potentiometrically or with an oxidation-reduction indicator. If vanadium is present in the steel, as is very often the case, vanadic acid is formed in the oxidation process, and this substance is titrated along with the chromic acid. It is necessary, then, to determine vanadium before the percentage of chromium can be estimated.

The desirability of the direct determination of chromium and of vanadium in steels has led to the suggestion of a number of methods, among which the following may be mentioned:

1. The excess of ferrous sulfate, remaining after the reduction of the chromic and vanadic acids, and the vanadyl salt may be titrated with standard permanganate (*5*). The accurate determination of this end point is difficult, especially if there is a large quantity of chromic salt in the solution, and a blank correction of rather indefinite value must always be applied. This titration has been made potentiometrically (*3*), but such a method cannot be recommended because of the very unsatisfactory character of the end point. If excess of ferrous sulfate is next added to reduce the slight excess of permanganate and the vanadic acid, and the excess removed by ammonium persulfate (*1*), a back-titration of the vanadyl salt with standard permanganate affords a method of obtaining vanadium on the same sample. The same difficulty with the end point, however, is encountered in this titration also.
2. Chromic acid may be titrated in the presence of vanadic acid with standard arsenite solution, the end point being determined potentiometrically (*13*). A very small amount of manganese must be present as catalyst, but the larger amounts usually present in steels lead to low results for chromium. All but a trace of manganese must be removed, therefore, before the titration, and it is desirable to remove most of the iron. After the chromium has been determined, the vanadic acid may be titrated potentiometrically in the same solution. Such a method for these elements is, obviously, not rapid.
3. After chromic and vanadic acids have been reduced with excess ferrous sulfate, the latter may be titrated potentiometrically at room temperature with standard ceric sulfate. The temperature of the solution is then raised to 70° to 75° C. and the vanadyl ion titrated potentiometrically with the same oxidizing agent (*11*).
4. Chromic acid may be reduced selectively in the presence of vanadic acid by a measured excess of standard arsenite (*2*). The excess of arsenite as well as any trace of vanadium which may have been reduced is titrated with standard permanganate, and a direct determination of chromium thereby obtained. The end point which is determined visually is described as satisfactory; a blank correction is required. A drop of arsenite is then added to the solution to reduce the slight excess of permanganate and the vanadic acid is titrated with standard ferrous sulfate, using diphenylbenzidine as an oxidation-reduction indicator. The results listed by the authors for chromium and vanadium in standard steels indicate that this method for chromium is fairly accurate.
5. Lang and Kurtz (*4*) have described a number of procedures for chromium and vanadium. Their results on steels, however, are not compared with those obtained by standard methods.

It is evident that direct indicator methods for chromium and for vanadium which are rapid and exact are needed, and the object of the present investigation has been to develop such methods.

Theoretical Considerations

From the reactions:

$$Fe^{++} \rightleftarrows Fe^{+++} + e$$
$$\text{and } VO^{++} + 2H_2O \rightleftarrows VO_3^- + 4H^+ + e$$

one would conclude that the oxidation potential of the ferric-ferrous system should not be appreciably influenced by a change in hydrogen-ion concentration of the solution, whereas that of the vanadate-vanadyl system should be considerably altered under similar conditions. Figure 1 illustrates this point for the latter system.

With an indicator of such high oxidation potential that it is not oxidized by vanadic acid, it should be possible in a mixture of ferrous, vanadyl, and chromic salts to obtain under proper experimental conditions two end points when titrating with a strong oxidizing agent. If the titration is commenced at room temperature in a solution of high hydrogen-ion concentration, the reaction between ferrous ion and the oxidizing agent should be rapid, while that between vanadyl ion and the oxidizing agent should be sufficiently slow, due to the lower reducing power of the vanadyl ion in such a solution, so that a good end point could be obtained when all ferrous ion is oxidized. This has been shown to be true when ceric sulfate is the oxidizing agent used in a solution 5 *M* in sulfuric

acid (*7*). In the following pages it will be shown that when permanganate is used, the same effect is obtained in a solution only 1 *M* in sulfuric acid. As the velocity of the reaction between vanadyl and permanganate ions is largely a function of the hydrogen-ion concentration of the solution and of its temperature, it should be possible, after reducing the acidity and raising the temperature of the solution, to titrate the vanadyl ion with permanganate, the indicator already present serving for this second end point.

o-Phenanthroline ferrous complex, an indicator of unusually high oxidation potential which has recently been described (*8*), appears to meet the necessary requirements, as it is not oxidized by vanadic acid in a moderately acid solution and is sufficiently stable for use at a temperature as high as 50° C. The indicator is red in color in reduced form and a very pale blue in oxidized form.

The experimental work which follows substantiates these theoretical considerations and shows their applicability to direct indicator methods for both chromium and vanadium in steel.

Experimental Methods for Steels without Tungsten

Reagents and Solutions. The 0.05 *N* potassium permanganate was standardized by potentiometric titration against sodium oxalate from the U. S. Bureau of Standards.

The ferrous sulfate solution, prepared either from ferrous sulfate or from ferrous ammonium sulfate, contained 20 cc. of sulfuric acid (specific gravity, 1.5) per liter and was standardized each day against the 0.05 *N* potassium permanganate. If the perchloric acid method for chromium is used, the standardization of the ferrous sulfate should be carried out in a dilute perchloric acid solution with *o*-phenanthroline ferrous complex as indicator; with the permanganate-azide or persulfate method for chromium, the same titration should be made in a dilute sulfuric acid medium. A ferrous sulfate solution standardized by the former method was found to be 0.09949 *N*, and by the latter method 0.09919 *N*. This discrepancy, which is probably due to the fact that the indicator dissolves only slowly in the perchloric acid solution, is insignificant except with small samples of steels of high chromium content, and in any event disappears if the proper acid medium is used in standardizing the ferrous sulfate.

Since, in the reaction between *o*-phenanthroline and ferrous ion, three molecules of the former combine with one of the latter, a 0.025 *M* solution of the indicator may be prepared by dissolving the correct amount of *o*-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) in a 0.025 *M* aqueous solution of ferrous sulfate. Ordinarily two drops of this 0.025 *M* indicator solution are sufficient to afford a very sharp color change in steel analyses.

Perchloric Acid Method. This method for chromium in steels without tungsten has been developed by Willard and Gibson (*9*). Their procedure, using perchloric acid both as solvent and oxidizing agent, was followed. After the oxidation was complete, the solution was cooled quickly,[1] diluted somewhat, boiled to remove chlorine, and then diluted further and cooled in running water. Experiments showed that after a measured excess of ferrous sulfate had been added to reduce the chromic and vanadic acids, the ferrous sulfate alone could be titrated at room temperature with standard permanganate, with *o*-phenanthroline ferrous complex as indicator, and a rapid and very sharp end point obtained, because at this acidity and temperature the reaction between vanadyl and permanganate ions is quite slow. If the hydrogen-ion concentration of the solution is then reduced by adding sodium acetate, and the temperature raised to 50° C., the red color of the reduced indicator returns and the vanadyl ion is easily titrated with further permanganate solution. A temperature of 50° C. seemed most satisfactory, for at higher temperatures too much of the indicator was destroyed, while at much lower temperatures the reaction was not sufficiently rapid. The end point in this second titration was considered as reached when the solution was a clear bluish green in color and when there was no return of any pink color after an interval of a minute. From the total volume of permanganate solution used, the percentage of chromium may be calculated directly, and from the difference between the first and second volumes of the permanganate, the percentage of vanadium may be determined. Obviously this procedure, which affords a determination of both chromium and vanadium in one sample, is very rapid—not more than a half-hour is required to weigh and prepare samples for the final

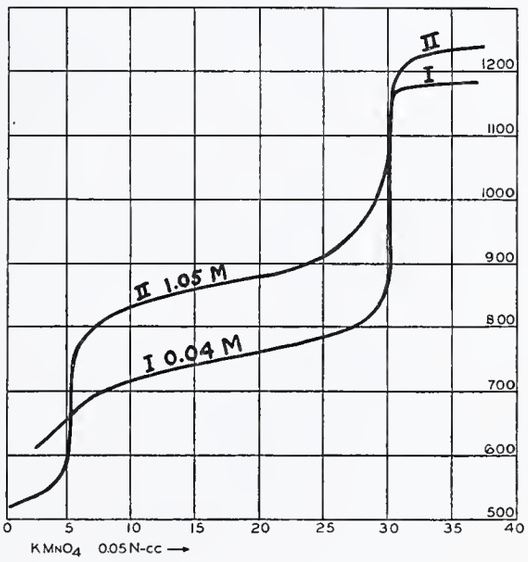

Figure 1. Titration of Mixture of Ferrous Sulfate and Vanadyl Sulfate with Potassium Permanganate

Solution I, 0.04 *M* in sulfuric acid; solution II, 1.05 *M* in sulfuric acid; temperature, 25° C.

titration. This method has the further advantage of giving an excellent end point at room temperature in the first step in the titration, while with the permanganate-azide or persulfate method either considerable acid must be added or the solution cooled to 5° to 6° C. before the titration of the excess ferrous sulfate. If the amount of vanadium is so small that large samples must be taken, the color of the chromic salt will be so intense as to render the end point indistinct. Results obtained on a number of steels by the perchloric acid method are given in Table I.

Table I. Direct Determination of Chromium and of Vanadium in Steels without Tungsten. Perchloric Acid Method

Steel		Samples I	II	III	IV
		%	%	%	%
B. S. 30 (*c*)	Cr	0.973	0.971	0.972	0.973
(0.977% Cr; 0.235% V)	V	0.234	0.239	0.237	0.237
B. S. 30 (*a*)	Cr	1.022	1.024	1.024	1.025
(1.02% Cr; 0.20% V)	V	0.208	0.201	0.201	0.203
Cr-V Steel*	Cr	0.917	0.925	0.919	0.920
(0.918% Cr; 0.134% V)	V	0.140	0.142	0.142	0.137
B. S. 72 (0.911% Cr; 0.012% V)	Cr†	0.917	0.918	0.918	0.916
B. S. 73 (13.93% Cr; 0.034% V)	Cr	13.89	13.85	13.84	13.94

* Chromium plus vanadium determined after persulfate oxidation by titration with ferrous sulfate, using diphenylbenzidine as indicator (*10*). Vanadium determined by permanganate-azide method (*12*).

† The vanadium is equivalent to 0.004 per cent of chromium and this value should be subtracted from each of those listed to obtain the correct percentage of chromium.

Two-gram samples of the first four and 0.25-gram samples of the last steel were used. The titration was made only to the first end point in analyzing the last two steels.

Recommended Procedure, Perchloric Acid Method. Weigh a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels, into a 500-cc. lipped beaker of tall form or into a 500-cc. Soxhlet flask. If the latter is used, the watch glass should be placed on very thin glass hooks

[1] G. F. Smith in a private communication to the authors has pointed out the desirability of cooling the solution quickly to prevent any reduction of chromium, which may be caused by the per-acid properties of the perchloric acid in a hot, concentrated solution.

or on a bent platinum wire about 1 mm. in diameter to prevent the formation of a liquid seal when the contents of the flask are heated. Add 20 to 25 cc. of 70 per cent perchloric acid (depending on the size of the sample) and heat very slowly to prevent the reaction from becoming violent. After the steel has dissolved (usually only 3 to 5 minutes will be required) boil the solution for 15 to 20 minutes. The longer period is better for high-chromium steels. Cool the flask and contents a moment in the air and then in a stream of running water. Add 25 cc. of water, rinse off the watch cover into the beaker, and boil the solution for 3 minutes to remove all chlorine. Dilute the liquid to 250 to 300 cc. and cool in running water. If the steel contains more than a trace of vanadium so that two end points are to be determined in the titration with standard permanganate, 15 cc. of phosphoric acid (specific gravity, 1.37) are added most conveniently at this point. Add to the solution at room temperature a measured excess of 0.1 *N* ferrous sulfate, and then two or three drops of 0.025 *M* *o*-phenanthroline ferrous complex. Much of the indicator precipitates, but sufficient of it is dissolved for the first end point and all of it dissolves on heating the solution before the second titration is commenced.

Titrate immediately after the addition of the indicator with 0.05 *N* potassium permanganate until the color of the solution changes from pink to a clear green. The end point is very sharp and there is almost no return of the pink color for a minute or more. Add sufficient crystallized sodium acetate to react with the free perchloric acid present. The amount of this salt required may be estimated approximately by considering that 5.4 cc. of 70 per cent perchloric acid are used to decompose and oxidize each gram of steel and that 1.6 grams of the acetate will be required for each cubic centimeter of the acid remaining. If preferred, the acetate may be added in small portions to the solution while it is being heated, until the addition of further acetate would cause the formation of a permanent precipitate of ferric phosphate. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl ion at once with the 0.05 *N* permanganate. The oxidizing agent should be added slowly, as only a small volume of it will be required and also because the reaction between vanadyl and permanganate ions is not instantaneous. The color change at the end point is the same as in the first titration and the end point is considered as reached when there is no return of a pale pink shade during an interval of a minute. It is sometimes advisable to add a drop more of indicator before titrating the vanadium.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 to 15 cc. of 70 per cent perchloric acid. Add 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

Permanganate-Azide and Persulfate Methods. In a previous paper (*12*) the authors have pointed to the possibility of using sodium azide to destroy all permanganate and thus of avoiding a filtration in the permanganate method (*6*) for chromium plus vanadium in steels without tungsten. Since the procedure for the permanganate method in this modified form is shorter than that for the persulfate method, it seemed important to ascertain the conditions under which the former might be used for the direct determination of chromium or of both chromium and vanadium on the same sample.

Samples of steel were dissolved in a mixture of sulfuric and phosphoric acids, and the ferrous salts and carbonaceous matter oxidized in the usual way with nitric acid. After dilution, the vanadyl and chromic salts were oxidized in hot solution with potassium permanganate, and the excess of the latter removed by careful addition of sodium azide to the boiling hot solution. All hydrazoic acid was removed by boiling, and the solution was then cooled in running water. A measured excess of ferrous sulfate was added at room temperature and an attempt was made to titrate the ferrous and vanadyl salts with a standard permanganate solution, using *o*-phenanthroline ferrous complex as indicator. After the ferrous sulfate was oxidized, the reaction, as was to be expected, became very slow. If the hydrogen-ion concentration of the solution was then reduced by the addition of sodium acetate and the temperature raised to 50° C., the vanadyl ion was easily titrated and a satisfactory end point obtained. The hydrogen-ion concentration of the solution may be reduced, if preferred, before any ferrous sulfate is added. The results for chromium on a number of steels which were analyzed in this way are recorded in the first column of Table II.

Since the oxidation by persulfate in the presence of silver ion is a standard procedure for chromium, analyses were made using this method. After the excess of persulfate had been removed by boiling, 1 to 3 hydrochloric acid was added to destroy the permanganate formed during the oxidation process, and the solution was then boiled to remove all chlorine. From this point the procedure was the same as that just given for the permanganate-azide method. Results are shown in the second column of Table II.

Experiments in which sodium azide was substituted for the hydrochloric acid after a persulfate oxidation (*12*) always led to high results for chromium. In such a procedure the silver ion is not precipitated, and may possibly cause interference later either by acting catalytically or as an oxidizing agent in the solution of low acidity. A study of the action of silver ion in synthetic mixtures similar to steels did not confirm either of these suppositions and the cause for high results here is still unexplained.

Table II. Direct Determination of Chromium in Steels without Tungsten. Permanganate-Azide and Persulfate-Hydrochloric Acid Methods

Steel	Method for Chromium $KMnO_4$-NaN_3	Method for Chromium $(NH_4)_2S_2O_8$-HCl
B. S. 30 (*c*) (0.977% Cr; 0.235% V)	0.970, 0.992, 0.980, 0.966	0.996, 0.981 0.985, 0.981
B. S. 30 (*a*) (1.02% Cr; 0.20% V)	1.04, 1.02, 1.02, 1.02	1.03, 1.05, 1.03, 1.03
B. S. 72 (0.911% Cr; 0.012% V)	0.908, 0.915, 0.912, 0.905	0.916, 0.920, 0.921, 0.931
B. S. 73 (13.93% Cr; 0.034% V)	13.95, 13.94, 13.93, 13.89 (13.85, 13.94, 13.88, 13.78)*	13.71, 13.79, 13.84, 13.87
B. S. 101 (17.54% Cr; 0.044% V; 8.44% Ni)	17.56, 17.60, 17.54, 17.51	17.42, 17.66, 17.58, 17.52
B. S. 64 (67.9% Cr; 0.11% V)	67.83, 67.83	

* After the steel had dissolved, vanadium equivalent to 2.5 per cent was added and the usual permanganate-azide procedure followed.

Two-gram samples of the first three steels, 0.25-gram samples of the fourth and fifth, and an aliquot portion of a 0.5-gram sample of the last were used.

Because of the low percentage of vanadium in Nos. 72, 73, 101, and 64 (as compared with the chromium content), it is unnecessary to reduce the hydrogen-ion concentration of the solution or to raise the temperature before the end point is reached. In fact, the ferrous sulfate must be titrated at room temperature and the volume of permanganate for this titration may be considered the final volume.

Table III. Effect of Varying Acidity on Determination of Chromium

H_2SO_4 Sp. Gr. 1.5	H_3PO_4 Sp. Gr. 1.37	Fe	V	$NaAc\cdot 3H_2O$	$FeSO_4$ 0.05 *N*	$KMnO_4$ 0.05 *N*	Chromium Present	Chromium Found
Cc.	*Cc.*	*Gram*	*Gram*	*Gram*	*Cc.*	*Cc.*	*Gram*	*Gram*
6	0	0	0	0	20	15.54	0.02252	0.02244
6	0	0	0	15	20	15.82	0.02252	0.02221
6	10	0	0	0	50	16.09	0.07505	0.70507
6	10	0	0	15	50	16.36	0.07505	0.07482
6	10	1	0	0	20	15.56	0.02252	0.02242
6	10	1	0	15	20	15.87	0.02252	0.02215
6	10	1	0.005	15	20	15.84	0.02252	0.02218
6	10	0.25	0.005	15	20	15.82	0.02252	0.02221

In the analysis of steel 64, results which were 0.4 to 0.5 per cent low were invariably obtained if the excess of ferrous sulfate was titrated in a solution of low acidity. This error, which corresponds to 0.2 mg. of chromium for the size of sample used, would therefore be negligible for low-chromium steels.

To investigate this error a standard dichromate solution was treated with sulfuric acid, and in some cases with sodium acetate, phosphoric acid, ferric alum, chromic sulfate, and

vanadyl sulfate solutions before a measured excess of ferrous sulfate was added. The volume of the solution in every case after the addition of the ferrous sulfate was 300 cc. Two drops of 0.025 *M* *o*-phenanthroline ferrous complex were added and the titration with permanganate was carried out, the solution being heated to 50° C. after the ferrous sulfate had been oxidized if there was any vanadium present. The results of a number of experiments are given in Table III.

These experiments indicate that the error caused by titrating the ferrous and vanadyl salts with permanganate in a solution of low acidity is an absolute error and so small as to be negligible except in cases such as B. S. steel 64, where the chromium content is very high.

Only the permanganate-azide method was used in investigating the possibility of determining both chromium and vanadium on the same sample of steel, as this method is more rapid than the persulfate method. Steel samples were prepared as just described and the final solution containing chromic and vanadic acids was cooled in running water. If a measured excess of ferrous sulfate was added to such a solution, followed by two drops of the indicator, and the ferrous sulfate alone was titrated with permanganate, it was impossible to obtain an end point because the hydrogen-ion concentration of the solution was not high enough to make the rate of oxidation of the vanadyl ion by the oxidized indicator sufficiently low. Numerous experiments, however, indicated that a sharp end point could be obtained in the titration of the ferrous sulfate in either of two ways: by cooling the solution so that its temperature at the end of the titration was not above 6° to 8° C., or by titrating at room temperature after the addition of considerable sulfuric acid. The first method is preferable, as the hydrogen-ion concentration of the solution must in any case be reduced before the titration of the vanadyl salt. The necessary concentration of acid for a titration at room temperature is indicated in the procedure given later. In the analyses listed in Table IV, the temperature of the solution at the first end point was 6° to 8° C. The hydrogen-ion concentration was then reduced by adding sodium acetate and the temperature of the solution raised to 50° C. before the titration of the vanadyl salt was made.

Table IV. Direct Determination of Chromium and of Vanadium in Steels without Tungsten. Permanganate-Azide Method

Steel		Samples I	II	III	IV
		%	%	%	%
B. S. 30 (*c*)	Cr	0.972	0.977	0.977	0.973
(0.977% Cr; 0.235% V)	V	0.232	0.226	0.230	0.236
B. S. 30 (*a*)	Cr	1.019	1.028	1.030	1.015
(1.02% Cr; 0.20% V)	V	0.203	0.206	0.194	0.206

Recommended Procedure, Permanganate-Azide Method. Place a 2-gram sample in a 600-cc. beaker, add 15 cc. of water and 15 cc. of phosphoric acid (specific gravity, 1.37), and run in a measured volume of sulfuric acid (specific gravity, 1.83) from a buret. Allow 1.5 cc. of the latter for each gram of steel and 3 cc. excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid (specific gravity, 1.42) in small portions to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 cc. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen and dilute to 300 cc. A few small pieces of broken porcelain in the solution will prevent bumping later. Heat to boiling, add a 2 per cent permanganate solution until a deep purple color remains, and boil the solution for 2 minutes. Add 0.1 *M* sodium azide (do this in a hood) to the boiling hot solution until a few drops excess are present. It is very important that the solution be boiling hot during the addition of the azide, especially if manganese dioxide is present. The azide will destroy the permanganate color first. Then add further azide, drop by drop, while stirring constantly until the solution clears. Boil for 5 minutes to remove all hydrazoic acid and cool the solution in running water. From this point either of two procedures may be used if both chromium and vanadium are to be determined on the same sample:

A. After adding 10 cc. of sulfuric acid (specific gravity, 1.5), cool the solution in ice to 5° C. or lower. Add a measured excess of 0.1 *N* ferrous sulfate and two drops of 0.025 *M* *o*-phenanthroline ferrous complex. Titrate the ferrous sulfate at once with 0.05 *N* permanganate solution. The change in color from pink to a clear green at the end point is very sharp. In a short time, however, the pink shade begins to return. To reduce the hydrogen-ion concentration of the solution, add slowly while stirring 10 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate until more would cause a permanent precipitate of ferric phosphate. Twenty grams will be found the correct amount if the quantity of sulfuric acid specified above has been used. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl salt at this temperature with the standard permanganate. (See procedure under the perchloric acid method for the precautions to be observed and the character of the end point.)

B. To the solution at room temperature to which 35 cc. of sulfuric acid (specific gravity, 1.5) have been added, add a measured excess of 0.1 *N* ferrous sulfate, and proceed as directed under *A*. The first end point is sharp here but less permanent as the pink color of the indicator appears again much more quickly, owing to its reduction by the vanadyl salt. Add slowly, while stirring, 25 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate as in *A*. Approximately 30 grams will be required. Proceed from this point as directed under *A*.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 cc. of sulfuric acid (specific gravity, 1.5). Add 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

If only chromium is to be determined, cool the solution containing chromic and vanadic acids in running water and reduce the hydrogen-ion concentration by adding crystallized sodium acetate as in *A* above. Add a measured excess of 0.1 *N* ferrous sulfate, 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex, and titrate at room temperature with 0.05 *N* permanganate. If it is impossible to obtain an accurate end point, the presence of vanadium is indicated. In such a case heat the solution, after the ferrous iron has been titrated, to 50° C. and complete the titration as directed in *A*. If a sharp and permanent end point is obtained at room temperature, heat the solution as usual to 50° C. to determine whether there is any return of the pink color. If there is, complete the titration of the vanadyl salt at 50° C. with the permanganate. If no pink color appears in the solution on heating, the end point obtained at room temperature is considered the final end point. In such a case, the acidity of duplicate samples of the same steel should not be decreased before the titration with the standard permanganate.

Application of Methods to Steels Containing Tungsten

Attempts to develop an indicator method for the direct determination of chromium and of vanadium in chrome-vanadium-tungsten steels were not successful. If the tungsten was kept in solution as a complex fluoride and the persulfate–hydrochloric acid method was used to obtain chromic and vanadic acids (*12*), it was found that, after the addition of a measured excess of ferrous sulfate, the determination of the excess of this reducing agent by titration with standard permanganate was not satisfactory, as the color change at the end point was not sharp. Quantitative results can be obtained in this titration if the solution is cooled to 5° to 8° C., or if the acidity is high, but the direct titration of the chromic and vanadic acids in such a solution with standard ferrous sulfate, using oxidized diphenylamine sulfonic acid as indicator, is much to be preferred, as in this case a very sharp end point is obtained. As was to be expected, it was impossible in continuing the titration with permanganate to obtain an end point in the titration of the vanadyl salt, because of the formation of a complex manganic fluoride.

When phosphoric acid was used instead of hydrofluoric acid to keep the tungsten in solution, a dark brown color developed upon the addition of excess ferrous sulfate. This color, which was caused possibly by a complex phosphovanado-tungstic acid, disappeared only slowly when permanganate was added to the solution. An end point when

all ferrous and vanadyl ions were oxidized could not be detected.

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Iodine Value of Rubber and Gutta-Percha Hydrocarbons

As Determined by Iodine Chloride

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The reactivity of various halogens towards rubber and gutta-percha hydrocarbons has been studied quantitatively. The behavior of both hydrocarbons toward halogens is very similar. The order of reactivity of the halogens is chlorine, bromine, iodine chloride, iodine bromide, and iodine. The results show that gutta-percha possesses a greater initial reactivity towards iodine than does rubber.

Data and detailed procedure are presented which offer further refinements to the iodine chloride method for the determination of the unsaturation of rubber and gutta-percha hydrocarbons.

Methods for the preparation of pure rubber and gutta-percha hydrocarbons are included and the corresponding iodine values found by the use of modified iodine chloride procedure are shown to be in close agreement with the theoretical.

It is recommended, in the case of gutta-percha hydrocarbon, that a greater excess of iodine chloride be used and that the reaction be carried on at room temperature for a longer period of time than that required for rubber.

Halogen absorption methods employing solutions of bromine, iodine bromide, or iodine chloride are widely used for determining the unsaturation of organic compounds. In the use of these methods the choice of halogen reagent, the amount employed, and the time and temperature for the reaction are all important factors which must be given careful consideration in order that the best results may be obtained. Certain structural differences in unsaturated organic compounds may have a decided influence on the reactivity of these substances toward halogens. For example, the presence of negative groups on one or both of the unsaturated carbon atoms protects against halogen addition; thus maleic or fumaric acids do not add iodine chloride (*7*). Styrene adds iodine chloride quantitatively, but in the case of cinnamic acid only a slight reaction takes place (*4*). No addition of iodine chloride occurs with dichloroethylene and very little with vinyl bromide (*3*). The authors have found that polyvinyl chloride (DuPrene) adds iodine chloride to only 30 per cent of theory. A triple-bonded compound, such as diphenylacetylene (*4*), shows only partial addition of iodine chloride, as would be expected from the negative effect of the first additive halogen. The unsaturated terpenes vary widely in their reactivity with halogens, extensive substitution occurring along with addition (*5*), particularly in the case of pinene. Aside from these complications, however, numerous investigators have shown that one or more of the halogens add quantitatively to a wide range of unsaturated hydrocarbons, acids, glycerides, alcohols, esters, etc. Of the many methods proposed the well-known Wijs procedure involving the use of 0.2 *N* iodine chloride in glacial acetic acid has been widely used and accepted.

In a previous investigation (*5*), various halogen absorption methods for determining the unsaturation of rubber and gutta-percha were studied and it was found that the Wijs reagent (iodine chloride in glacial acetic acid) was the most satisfactory for this purpose. It was shown that under suitable conditions iodine chloride adds quantitatively to the double bonds in rubber hydrocarbon in close agreement with theory—i.e., one molecule of iodine chloride adds to each C_5H_8 grouping. This is equivalent to a theoretical iodine value of 372.8 and values found by the iodine chloride method for pure rubber hydrocarbon agree to within less than 0.5 per cent of this figure.

The method previously described (*5*) involves swelling 0.10-gram samples of rubber, etc., in 75 cc. of carbon bisulfide, adding 25 cc. of 0.2 *N* iodine chloride in glacial acetic acid, allowing the solution to stand 2 hours at 0° C., and titrating the excess iodine chloride with 0.1 *N* sodium thiosulfate immediately after addition of potassium iodide solution, using starch as the indicator. Excellent results were also obtained by allowing the reaction to proceed at room temperature for one hour, although substitution occurred slowly at this temperature. Since conducting the reaction under ice-cooling is a troublesome feature, one of the purposes of the present investigation was to determine the best conditions for operating at room temperature without sacrifice in the accuracy of the method. Another related objective was to determine if any differences exist between rubber and gutta-percha hydrocarbons with respect to their reactivity towards iodine chloride and other halogens. This phase of the study is of

particular interest with respect to the chemistry of these complicated hydrocarbons.

Since its publication, the original method (*5*) has been employed by numerous investigators to determine the purity as well as to follow the changes in unsaturation of rubber and gutta-percha when these substances were subjected to various treatments. Staudinger and Bondy (*12*) have followed the reduction in iodine value and thereby the cyclization of rubber and gutta-percha when subjected to elevated temperatures in various solvents. Fisher and McColm (*1*) treated rubber with sulfuric and sulfonic acids and determined the reduction in unsaturation using the iodine chloride method. The effect of high tension alternating currents in producing cyclization has been correspondingly studied by Fromandi (*2*). Kemp, Bishop, and Lasselle (*6*) similarly followed the change in unsaturation resulting from oxidation of rubber and gutta-percha hydrocarbons.

Materials

The rubber hydrocarbon employed for this work was prepared by repeatedly extracting 10 grams of pale crepe at room temperature with 100 cc. of a mixture of three parts acetone and one part C. P. petroleum ether (boiling point, 35° to 52° C.) in order to insure thorough removal of the resin. The acetone was removed by washing quickly with petroleum ether and the rubber was then covered with 1000 cc. of the same solvent. As a precaution against oxidation, an atmosphere of carbon dioxide was maintained over the surface of the solution. After 10 days' storage at room temperature in a dark cabinet the petroleum ether solution of rubber was decanted from the gel and about 90 per cent of the solvent distilled off. The remainder of the solvent was removed with a stream of carbon dioxide at room temperature and finally by heating in a vacuum (0.1 mm. residual pressure) at 50° C. until a constant weight was attained. The product was colorless, crystal clear, tough, and elastic. Analyses indicated the absence of ash and nitrogen.

Table I. Reactivity of Various Halogens with Rubber and Gutta-Percha Hydrocarbons[a]

Hydrocarbon	Halogen Used	Reaction Period	Reaction Temperature	Iodine Value	Unsaturation
		Hrs.	*° C.*		*%*
Rubber	Cl_2	3	0	570	153
Rubber	Br_2	0.5	0	399	104
Rubber	Br_2	3	0	421	113
Rubber	I_2	3	0	1.3	0.35
Rubber	ICl	2	0	371.0	99.5
Gutta (Pahang)[b]	ICl	2	0	366.4	98.3
Rubber	IBr	0.5	0	286	76.7
Rubber	IBr	16	0	326	87.4
Gutta (Pahang)	IBr	0.5	0	292	78.3
Gutta (Pahang)	IBr	16	0	324	86.9
Gutta (Balata)	IBr	0.5	0	292	78.3
Gutta (Balata)	IBr	16	0	324	86.9
Gutta (Balata)	IBr	3	25	316	84.7
Rubber	I_2	0.16	25	1.08	0.29
Rubber	I_2	1	25	4.55	1.22
Rubber	I_2	3.125	25	9.20	2.47
Rubber	I_2	7	25	15.6	4.18
Rubber	I_2	18	25	23.7	6.36
Rubber	I_2	40	25	27.9	7.47
Gutta (Balata)	I_2	1	25	6.74	1.81
Gutta (Balata)	I_2	3.25	25	14.8	3.97
Gutta (Balata)	I_2	7.1	25	17.6	4.71
Gutta (Balata)	I_2	18	25	23.2	6.22
Gutta (Balata)	I_2	40	25	26.8	7.18

[a] A 0.10-gram sample of hydrocarbon was dissolved in 75 cc. of C. P. carbon disulfide, and 25 cc. of the 0.2 *N* halogen in glacial acetic acid were added. At the end of the reaction period, after the addition of 15 per cent aqueous KI, the excess halogen was titrated with 0.1 *N* $Na_2S_2O_3$, using starch as the indicator. The flasks were kept in the dark during the reaction period.

[b] See Kemp, Bishop, and Lasselle (*6*) for method of preparation. Carbon (found) 87.82 per cent; (theory) 88.15 per cent. Hydrogen (found) 11.73 per cent; (theory) 11.85 per cent.

Balata hydrocarbon was prepared separately from samples of both the "red" and "white" latices representing two common varieties of the *Mimusops Balata* which were obtained by Weise and Company of Rotterdam. In each case the balata was coagulated by adding an excess of 50 per cent alcohol to the latex. The coagulum was washed in hot 50 per cent alcohol, then in hot water, and finally was dried in vacuum over calcium chloride. The resin was removed by repeated extraction with petroleum ether (boiling point, 35° to 52° C.) and the gutta was then dissolved in carbon disulfide, carbon dioxide being used to replace the air over the solution. After about 1 week the insoluble matter had completely settled, leaving a water-white clear solution of gutta which was decanted. The gutta was then precipitated with absolute alcohol. The alcohol was removed from the gutta by washing with petroleum ether and the absorbed petroleum ether evaporated in a stream of carbon dioxide. The hydrocarbon was finally heated to constant weight in a high vacuum at 60° C. In this connection it was observed that the last traces of solvent were more difficult to remove from the gutta than from the rubber hydrocarbon. The resulting product was milky white at room temperature and softened at 61° C., finally becoming colorless and crystal clear at 70° C. The product was free from ash and nitrogen.

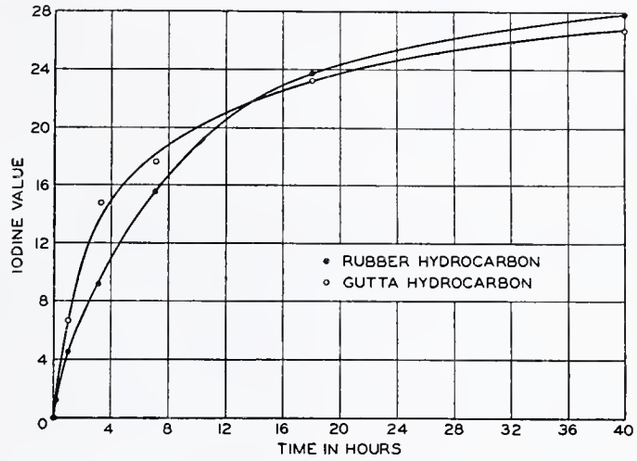

Figure 1. Rate of Reaction of Iodine with Rubber and Gutta-Percha Hydrocarbons

Reactivity of Halogens with Rubber and Gutta-Percha Hydrocarbons

Although some data were presented in the earlier publication (*5*) to illustrate the relative reactivity of various halogen solutions toward rubber, the data shown in Table I are more complete and include experiments with gutta-percha hydrocarbon. This information is of particular interest because of the relationship shown between rubber and gutta-percha hydrocarbons in their reactivity towards iodine chloride, iodine bromide, and iodine.

The most significant difference between these hydrocarbons in respect to their reactivity with halogens is the more rapid initial reaction of gutta with iodine as shown by the results in Table I which are plotted on Figure 1. Further evidence on this point has been obtained in connection with the separate refluxing of 10 grams of crepe rubber and gutta in 100 cc. of tetrachloroethane for 10 hours in an atmosphere of carbon dioxide. The gutta was found to undergo extensive cyclization as shown by a reduction in iodine value to 247, while rubber remained practically unchanged with an iodine value of 344. Staudinger and Bondy's (*12*) results also indicate that gutta-percha has a greater tendency to cyclize than does rubber.

The results in Table I also clearly show the superiority of iodine chloride as compared with other halogens for use in determining the unsaturation of rubber and gutta-percha hydrocarbons.

Gorgas (*3*) found that the activity of iodine bromide was

Table II. Iodine Value of Rubber Hydrocarbon

(Using 0.2 *N* iodine chloride in carbon tetrachloride followed by McIlhiney (*8*) procedure)

Number	Weight of Sample	Rubber Solvent Used $CHCl_3$	Reaction Period	Reaction Temperature	Excess of 0.2 *N* ICl in CCl_4 Used	Total Iodine Value	Additive Iodine Value	Substitutive Iodine Value	Total Unsaturation
	Gram	*Cc.*	*Hrs.*	° *C.*	%				%
1	0.1432	75	6	0	17	369.6	359.6	9.9	99.1
2	0.1419	75	6	25	17	371.1	347.2	23.9	99.5
3[a]	0.1000	50	6	22	22	369.1	326.8	42.3	99.0
4[a]	0.1000	50	6	22	22	371.6	323.6	48.0	99.6
5	0.1000	50	6	22	22	373.0	310.7	62.7	100.1
6	0.1000	50	6	22	22	374.5	317.9	56.7	100.4
7	0.1355	100	6	0	24	372.0	350.0	22.2	99.7
8	0.1356	100	6	0	24	370.6	348.4	22.2	99.4
9	0.1052	75	2	0	60	381.5	342.7	38.7	102.3
10	0.1032	75	2	21	62	391.4	348.9	42.4	104.9

[a] Solid KI added according to Pummerer and Stärk (*10*).

increased by substituting carbon tetrachloride for glacial acetic acid as a solvent and by employing a larger excess of iodine bromide. In this connection, he recommended determining the iodine value of rubber by adding a large excess (50 cc. of 0.2 *N*) of iodine bromide in carbon tetrachloride to 0.15 gram of rubber in the same solvent and conducting the reaction at room temperature for exactly 15 minutes. He found that excessive consumption of halogen occurred if longer periods were used. The authors obtained low iodine values (316) for rubber when employing the Gorgas procedure; but by using 0.1 gram of rubber, 50 cc. of 0.2 *N* iodine bromide, in carbon tetrachloride, and 30 minutes at room temperature were able to obtain more consistent results. It was found, however, that under these conditions the results were variable and could not be relied upon where a high degree of accuracy was necessary.

Use of Iodine Chloride in Carbon Tetrachloride

Pummerer and Mann (*10*) determined the unsaturation of sol and gel rubber by adding iodine chloride in carbon tetrachloride to a chloroform dispersion of the rubber and allowing the solution to stand at room temperature for various intervals of time. These authors state, but do not show, that it is immaterial whether the various kinds of rubber are

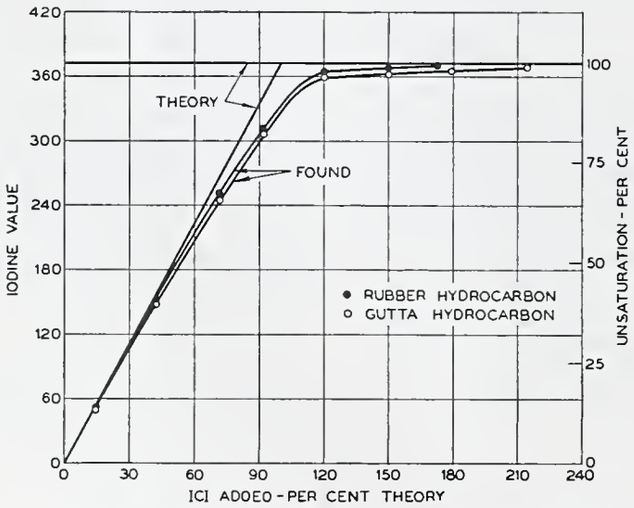

Figure 2. Effect of Amount of Added Iodine Chloride on Iodine Value of Rubber and Gutta-Percha Hydrocarbons

tested in the chloroform solution at 0° C. or at room temperature, whether they are left to stand for 6 or 96 hours, and whether 0.7 per cent or 0.2 per cent solution of rubber is treated. Although results on tests run at 0° were not published, their data showed that considerable substitution occurred at room temperature, gel rubber, for example, showing an unsaturation value 10 per cent in excess of the theoretical. It was stated that chloroform has the advantage over carbon disulfide in that cooling is unnecessary, but no results were given to support this contention. Later, Pummerer and Stärk (*11*) found that more consistent results could be obtained by limiting the excess of iodine chloride to 10 to 20 per cent and the reaction period to 6 hours at room temperature. Increased substitution was found to occur when more than the 20 per cent excess of iodine chloride was used. Their results were in good agreement with theory. However, when corrected for halogen acid present at the end of the reaction, as a gage of the extent of substitution, the values were in some cases as much as 6 per cent below the theoretical. Halogen acid was estimated by direct titration with sodium hydroxide following the titration with sodium thiosulfate.

The authors have carried out a series of experiments similar to those of Pummerer and Stärk (*11*) except that the liberated halogen acid was determined by the well-known McIlhiney (*8*) procedure involving the addition of potassium iodate solution immediately after the first titration with 0.1 *N* sodium thiosulfate. The iodine liberated by the halogen acid was then titrated with the sodium thiosulfate. Pure sol rubber hydrocarbon prepared by diffusion into petroleum ether from acetone extracted crepe was employed for these determinations. This preparation was transparent, colorless, and free from ash. The results given in Table II are in good agreement with those of Pummerer and Stärk, except that larger quantities of halogen acid were liberated. The close agreement of the total iodine values with theory is an indication that the halogen acid is formed largely as a result of hydrolysis of the rubber iodochloride addition product and not from substitution. Ingle (*4*) has noted that certain iodochlorides can be readily hydrolyzed. In the presence of too great an excess of iodine chloride, substitution apparently does occur at both 0° and 25° C. and is manifested by total iodine values which are higher than the theoretical.

When compared with the modified Wijs procedure as previously described (*5*), the method of Pummerer and Stärk appears to have certain disadvantages. For example, 6 hours are required as compared with 1 or 2 for the Wijs solution. The end points are not sharp and the variations in results therefore somewhat greater. Close attention must be paid to the amount of excess iodine chloride used, whereas with iodine chloride in glacial acetic acid variations of 70 to 200 per cent give practically the same results and the time of reaction is not so critical. In glacial acetic acid the solution of iodine chloride is more stable and permits of easier manipulation with less danger of loss of halogen due to volatilization than when carbon tetrachloride is used as the solvent. Hydrolysis of the iodochloride is undoubtedly a disturbing factor in the Pummerer procedure, but the use of a glacial acetic acid solution of iodine chloride in conjunction with carbon disulfide as the rubber solvent seems to exert a powerful repressing influence on side reactions such as substitution and hydrolysis.

The use of the McIlhiney or Pummerer procedure is of

advantage in case one wishes to determine the extent of substitution and hydrolysis by estimating the halogen acid split off during the reaction. This advantage was pointed out in the earlier publication by Kemp (*5*), particularly with respect to the study of the reaction of various terpenes with halogens.

Effect of Time and Temperature

It was previously shown (*5*) in the case of pure rubber hydrocarbon at 0° C. that reaction periods ranging from 1 to 20 hours had no effect on the resulting iodine values and that these latter were equivalent to 99.7 per cent of the theoretical. The iodine value found for 15-minute periods at room temperature was the same as the 20-hour period at 0°, but after 20 hours at room temperature the iodine value rose to 102.3 per cent of theory. Since no similar data were obtained for gutta hydrocarbon at that time, it was decided to investigate the effect of time and temperature on the iodine value of gutta-percha. Further study was also made on the accuracy of results obtained with rubber for the shorter periods at room temperature since this procedure has manipulative advantages over the one previously recommended in which 2 hours at 0° C. was employed. These results are shown in Table III.

Table III. Effect of Time and Temperature on Iodine Value of Rubber and Gutta Hydrocarbon[a]

Hydrocarbon	Weight of Sample	Reaction Period	Reaction Temperature	Iodine Value	Unsaturation
	Gram	*Hrs.*	*° C.*		*%*
Rubber	0.0798	1	25	372.1	99.81
	0.0798	1	25	371.8	99.70
	0.0798	1	25	371.7	99.68
Rubber (*4*)	0.1033	1	0	371.7	99.68
Rubber (*4*)	0.1024	1	0	371.2	99.57
Balata (red)	0.0999	1.25	25	366.1	98.20
Balata (white)	0.1012	1.25	25	365.8	98.12
Balata (red)	0.0502	1.33	25	368.2	98.76
Balata (white)	0.0507	1.33	25	369.1	99.01
Balata (red)	0.0503	2.33	25	370.0	99.24
Balata (white)	0.0510	2.2	25	372.0	99.79
Balata (red)	0.0857	2	0	364.2	97.69
Balata (red)	0.0855	2	0	363.2	97.42
Balata (red)	0.1011	2	0	362.3	97.18
Balata (red)	0.0998	2	0	362.2	97.16

[a] Hydrocarbon dissolved in 75 cc. of CS_2 and 25 cc. of 0.2 *N* iodine chloride in glacial acetic acid added.

In determining the iodine value of balata hydrocarbon by the modified Wijs method at 0° C. it was noted that upon cooling, after the addition of the iodine chloride, a finely divided precipitate separated out. This precipitation does not take place with rubber. If room temperature is employed when determining the unsaturation of gutta-percha, precipitation is avoided. As can be seen from the results in Table III, gutta-percha appears to require a greater excess of Wijs reagent and a longer period of time for the completion of the reaction than does rubber. The use of a 0.05-gram sample and 25 cc. of Wijs solution for a 2-hour period at room temperature appears to be suitable for determining the iodine value of gutta-percha hydrocarbon. These results indicate that gutta-percha hydrocarbon does not absorb iodine chloride as rapidly as rubber hydrocarbon during the latter stages of the reaction.

In order to determine the relative rates of reaction of rubber and gutta-percha hydrocarbon with iodine chloride, 0.5000-gram samples of each were dissolved in 500 cc. of carbon disulfide in a volumetric flask, 50-cc. portions were pipetted into iodination flasks, and varying quantities of 0.2 *N* Wijs solution were added from a buret. The flasks were allowed to stand 10 minutes in the dark at 25° C. and the unreacted iodine chloride was determined by titration with 0.1 *N* sodium thiosulfate after the addition of aqueous potassium iodide and starch solution. These results are given in Figure 2 and show that the gutta-percha requires a greater excess of iodine chloride for the completion of the reaction than the rubber hydrocarbon.

Recommended Procedures

Preparation of 0.2 *N* Wijs Solution. Thirteen grams of pure iodine in powdered form are dissolved in a liter of glacial acetic acid (Merck's highest purity) heated to between 80° and 90° C. One hundred cubic centimeters of this solution are removed and set aside for use later. Chlorine gas, which has first been bubbled through water and then through concentrated sulfuric acid, is passed into the main portion of the iodine solution until the brown color changes to orange, at which time the passage of the chlorine is quickly stopped. The 100-cc. portion of iodine solution is now added to the main portion of iodine solution until a faint brown color remains, indicating only a slight excess of free iodine. The solution is then heated at 80° to 90° C. for 20 minutes, allowed to cool, and placed in a glass-stoppered brown bottle. Great care must be exercised to avoid contact of this solution with moisture. All containers should be scrupulously clean and dry before being used. When prepared in this manner, the solution is very stable and will keep several months without change.

Preparation of 0.1 *N* Sodium Thiosulfate Solution. Twenty-five grams of pure $Na_2S_2O_3 \cdot 10H_2O$ are dissolved in a liter of boiled distilled water and kept in a ground-glass stoppered bottle. It is standardized against pure potassium biniodate, iodine, or potassium dichromate in the usual manner as described in textbooks on analytical procedure (*9*). The present authors prefer the use of pure iodine for this standardization.

Procedure for Determination of Iodine Value of Rubber, Gutta-Percha, Etc. In determining the iodine value or hydrocarbon content of crude rubber, balata, gutta-percha, or latex these substances must first be freed from moisture and resins. Tenth-gram samples (0.05 gram in case of gutta-percha) are placed in 500-cc. flared lipped ground-glass stoppered iodination flasks and covered with 75 cc. of carbon disulfide (Merck's highest purity). After standing overnight, 25 cc. of the 0.2 *N* Wijs solution are added from a pipet, while the flask is shaken so as to impart a rotating motion to the carbon disulfide solution during this operation. The solution should be clear and free from precipitate after addition of the iodine chloride. The stoppers are wetted with a drop of 15 per cent potassium iodide solution and the flask is placed in a dark place and allowed to stand for 1 hour (2 hours in the case of guttas). Twenty-five cubic centimeters of 15 per cent freshly prepared potassium iodide solution and 50 cc. of recently boiled and cooled distilled water are then added and the liberated iodine is titrated immediately with 0.1 *N* sodium thiosulfate. Toward the end of the titration 5 cc. of a freshly prepared 1 per cent solution of soluble starch are added as an indicator. The solution is rapidly rotated during titration and as the end point is approached, the color changes are from blue to brown to yellow. From this point on, the titration must proceed with caution. The solution should be shaken after the addition of every half drop and when the end point is reached the canary yellow color of the contents of the flask will fade out to a milky whiteness. A blank is run simultaneously with the sample. The difference in cubic centimeters of 0.1 *N* thiosulfate between the blank and sample titration is used to calculate the iodine value and per cent unsaturation in the following manner:

$$\text{Iodine value} = \frac{\text{cc. } 0.1\ N\ Na_2S_2O_3 \times 1.2692}{\text{wt. of sample in grams}}$$

$$\text{Unsaturation (per cent)} = \frac{\text{iodine value found}}{3.728}$$

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Testing Reclaimed Rubber

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A description and interpretation of physical tests on raw reclaimed rubber are presented. A discussion of the merits of tests on reclaim-sulfur cured compounds versus tests of typical compounds containing the reclaims shows that the former are of little value, except in the case of specific gravity. A testing procedure is recommended for the consumer of reclaimed rubber, which stresses processing and physical tests on cured compounds from a factory test run (preceded by laboratory tests only if they can be interpreted accurately), using a specific and suitable recipe.

A CONSIDERATION of the testing of raw material such as reclaimed rubber should include both the manufacturer's tests for control purposes and tests applied by the consumer to insure himself against variations in raw material purchases. These tests may be identical in many cases, but the consumer may also run actual processing tests in his product and factory.

All the larger rubber companies and most smaller ones with a technical staff run tests on incoming raw materials. The problem here is to determine the minimum number of tests involving the minimum of time and labor which will assure the consumer that his raw material is uniform and comparable to previous shipments. It is decidedly unfortunate and costly for both producer and consumer if the consumer's specification tests on many rubber compounding ingredients are incorrectly chosen, carelessly performed, and too critically interpreted. These faults may be found singly or together, and the technologist responsible for the condition may not be receptive to the introduction of new ideas. Any of the above conditions necessarily means unwarranted rejections, inconvenience, and expense.

The object of this paper is to evaluate both manufacturer's and consumer's tests applied to reclaimed rubber, and to suggest a simple, rational, and practical procedure for testing this compounding ingredient.

A résumé of the chemical and physical tests applied to reclaimed rubber is as follows:

I. Chemical Tests
  A. Raw or uncured reclaim
    1. Acetone extract
    2. Chloroform extract
    3. Alcoholic potash extract
    4. Total and free sulfur
    5. Carbon black
    6. Cellulose
    7. Alkalinity or acidity
    8. Moisture
    9. Ash
    10. Ash analysis
    11. Special tests—e. g., manganese, lead

II. Physical Tests
  A. Raw or uncured reclaim
    1. Manual or visual
    2. Smoothness
    3. Milling
    4. Tubing
    5. Plasticity and recovery
    6. Load capacity
    7. Color
  B. Reclaim cured with sulfur
    1. Specific gravity
    2. Tensile, elongation, and stress
    3. Permanent set
    4. Resistance to tear
    5. Rate of cure
  C. Reclaim in special test formulas
    1. Any usual cured rubber tests
    2. Any of the tests listed under II-A on the uncured compound

Generally speaking, chemical tests are run for the purpose of ascertaining the constituents of the reclaim for efficient compounding. These analyses in detail are supplied by the manufacturer as representative of his product. Occasionally purchasing specifications will limit some chemical constituents, such as manganese content or alkalinity. Inasmuch as most analytical procedures are or can be based on fundamental chemical methods, the figures are reproducible from one laboratory to another. While chemical tests and laboratory procedures are important, they are not, with few exceptions, usually a serious or much disputed factor in control testing as compared to physical tests. The results of chemical analysis are generally accepted as an innate characteristic of the reclaim, and are so used by compounders.

Physical tests must be classified according to the state of the reclaim when tested.

Raw or Uncured Reclaim

The processing of reclaimed rubber depends upon its condition in the raw state. Therefore, any tests which will indicate its processing qualitities are of great value.

A manual and visual test of reclaim should be the first and is the simplest test to which it may be subjected after manufacture or upon purchase. This is primarily a manufacturer's preliminary control method, but is, of course, applicable to qualitative differentiation of various types of reclaim. Depending upon the expertness of the inspector, this test reveals qualitatively the softness, nerve, color, odor, and smoothness of the product. In a given production run, an experienced inspector can very accurately eliminate material which is irregular and not comparable to a control. This test is most valuable as an index of smoothness.

The smoothness of a reclaim is easily noted by visual examination of slabs finished from refiners in thin sheets. However, for reclaims finished from slabbing mills in thicker sheets (0.010 to 0.025 inch, 0.25 to 0.62 mm.) some other test is necessary. Mixing the reclaim in equal quantity with clean smoked sheets offers the simplest method. When a sheet of this mixture is stretched thin with the fingers, the presence of any lumps will be revealed. Further, if a piece of the mixture about 2 cm. thick is cut while hot, the lumps will be pushed out in subsequent contraction upon cooling and will be visible on the outer surface. Another method is to mix 50 parts of reclaim with about 10 parts of mineral rubber and 40 parts of whiting, after which it is tubed. Any unrefined lumps will show upon the tubed surface.

The test of most value would be one for judging the processing qualities, and for this purpose, milling tests offer a great deal of information in a short time. Any laboratory can set up a procedure (*4*) suitable to its equipment for running this test, using a uniform volume of sample, roll setting, roll speed, number of cuts, and temperature. A general recommendation of a sheet 10 mm. (0.25 inch) in thickness, low bank, low speed, and cool rolls is made. Naturally a control should always be run. The number of minutes required to reach a definite degree of smoothness and to adhere to the back roll of the mill allows a numerical record. The former indicates inertness or speed of break-down preparatory to pigment incorporation and the latter indicates the degree of tackiness. This test can be of immense value in gaging nerve or inertness, and degree of tackiness.

Reclaim suitable for tubing work may be evaluated by extrusion through a 3.2-mm. (0.125-inch) die. Visual examination of the surface waviness indicates the comparative inertness. This test on a reclaim of high nerve such as first-grade alkali whole tire or tube reclaim is of little value, as these reclaims are very nervy and consequently show much waviness. These reclaims then must be loaded to give a smooth surface. After a definite period of rest (1 hour is sufficient) the sample may be gaged and the percentage of swelling calculated. Thus a definite numerical rating of this quality is obtained. A control is desirable for this test.

Table I. Plasticity and Milling Tests

Reclaim Type	Yield[a]	Recovery[b]	Milling Time To become smooth	Milling Time To adhere to back roll
	Mm.	*Mm.*	*Min.*	*Min.*
Boot and shoe, acid-alkali	7.12	1.90	0.5	5.0+
Whole tire, acid-alkali	6.09	2.99	0.8	5.0+
Whole tire, alkali	5.14	3.11	0.85	4.4
Solid tire, digester	6.36	2.88	0.6	3.3
Inner tube, digester	3.98	3.73	1.6[c]	5.0+
Inner tube, pan	3.54	2.46	2.6[c]	5.0+

[a] Williams (*7*) Y value.
[b] After 10 minutes.
[c] Difficult to interpret for tube reclaims.

Plasticity determinations on reclaimed rubber may be carried out on pieces cut directly from the slabs or by building up a laminated pellet from a calendered sheet as described by Winkelmann and Croakman (*9*). In this laboratory a great many tests have been run on reclaim slabs under various conditions, with the conclusion that the plasticity measurement as any sort of routine test is very variable for reclaimed rubber. Further, it measures only resistance to flow under load at a given temperature and load, and does not indicate much about processing qualities. The measurement of recovery, however, does indicate nerve very well, and in this respect coincides in order of magnitude with the smoothing time in the milling test. Table I shows typical figures on these tests for various types of reclaim. The boot and shoe reclaim, for example, has a very low plasticity (high numerical figure), and yet is the most inert, as is shown by the recovery and milling test. On the other hand, the plasticity and recovery tests on the compound in which the reclaim is used are very much more accurate, dependable, and useful.

The quantity of pigment which a reclaim will take up before crumbling is often important, and perhaps still more important is the speed of incorporation. The relative quantities of pigment which reclaims will absorb may be observed by incorporating first 100 per cent and then 25 per cent of its weight in whiting, continuing the addition of 25 per cent increments until the batch crumbles. Table II indicates how four typical reclaims behave under this test. The speed of incorporation may be recorded either by how much whiting or other pigment will be taken up in a given time or by how fast a given quantity is incorporated.

Table II. Loading Tests

Reclaim	Whiting Load
	%
Whole tire I	275
Whole tire II	225
Solid tire	175
No. 2 tube	275

The color of light grades of reclaimed rubber may be determined by matching the sample of reclaim against a control. In general it is necessary to dilute tube reclaims for a satisfactory color check. A simple recipe for this purpose is:

Pale crepe	50
Lithopone	25
Reclaim	25
	100

The crepe and lithopone are preferably master-batched for use. It is often desirable to use a mix of the specific color to be matched to achieve the most accurate comparisons.

Reclaim Cured with Sulfur

It is now standard practice for all tests of reclaim, cured with sulfur only, to use a ratio of 100 parts of reclaim to 5 parts of sulfur.

The specific gravity determination is the only property for which this mixing is really worth while. In the actual determination of the specific gravity, the use of solutions as balancing media is recommended as the most accurate, most readily kept under control, and also the most rapid method for routine work. For calculating the true specific gravity of the reclaim, the following formula is applicable, where A equals specific gravity of reclaim plus sulfur mix.

$$\text{True specific gravity} = \frac{100\,A}{105 - 2.41\,A}$$

The tensile strength and elongation of reclaimed rubber, as determined from the reclaim-sulfur mix, has long been considered by many as a prime index of its quality. This is a very unfortunate assumption, as will be shown.

The cures are generally made at 141.7° C. (287° F.), the times usually being between 15 and 35 minutes. The rate of cure problem has been extensively studied (*2*, *5*) and a reference to these papers will show the effect of time of cure. A cure of 25 minutes at 141.7° C. serves as a satisfactory standard of comparison for these tests.

For discussion of this test Table III is shown. One-half slab of each reclaim was cut into pieces and well blended on a mill. From this blend seven mixings with sulfur were made, two slabs from each mixing being cured 25 minutes at 141.7° C. Four strips from each slab were then tested, as described by Palmer (*3*). For both the alkali whole tire and neutral solid tire reclaim, a maximum deviation of 5 kg. per sq. cm. (70 lb. per sq. in.) in tensile strength and 35 and 25 per cent, respectively, in elongation is obtained.

Table III. Error in Physical Tests of Reclaim-Sulfur Mixes

Slab Number	Whole Tire Elongation	Whole Tire Tensile strength	Solid Tire Elongation	Solid Tire Tensile strength
	%	Kg./sq. cm.	%	Kg./sq. cm.
1	415	50	335	56
2	410	48	325	55
3	430	51	325	51
4	430	50	325	54
5	435	52	320	53
6	435	50	325	51
7	430	50	320	52
8	420	47	315	52
9	440	51	335	52
10	445	51	330	53
11	430	50	310	52
12	430	49	315	52
13	425	47	310	52
14	425	47	315	53
Average	429	49.5	322	52.7
Maximum variation	35	5	25	5

Testing temperature, 22.5° C.

If this numerical variation were based on a compound having a tensile strength of 211 kg. per sq. cm. (3000 lb. per sq. inch) and an elongation of 600 per cent, the percentage variation would be comparatively low, 2 to 3 per cent in tensile strength and 4 to 6 per cent in elongation. Based on the low tensile reclaim, however, the variation in tensile strength and elongation is approximately 10 per cent. These figures represent what is believed to be nearly a minimum variation in reclaim testing; therefore, one should not contract his critical judgment more than 10 per cent at most in examining reclaim-sulfur test figures. In many laboratories the general run of results will vary more than 10 per cent. If one desires to average the results from a sufficient number (minimum of 8) test strips (*3*), results of reproducible nature may be obtained. Assuming that such a test procedure is carried out, what meaning do the results have? Winkelmann (*8*) has stated, "There is a tendency to evaluate too much on tensile strength. The real significance of the tensile strength of a reclaim and its relation to the physical properties of the compound in which it is used have yet to be determined.... The reclaims which give a low tensile strength when cured with sulfur may, however, have the correct degree of disaggregation for yielding good results with rubber and other ingredients." In support of these statements, Winkelmann has shown the results of using three tube reclaims, three whole tire reclaims, and one carcass reclaim both in the reclaim-sulfur mix and in a friction compound containing 24 per cent of reclaim. While the reclaim-sulfur figures varied considerably, the stress-strain curves of the compounds were very close together. Specifically, two tube reclaims having tensile strengths, when cured with sulfur 25 minutes at 141.7° C., of (1) 1392 lb. per sq. in. and (2) 287 lb. per sq. in. showed, in his compound, maximum tensile strengths (from his curves) of (1) 2950 lb. per sq. in. and (2 3000 lb. per sq. in.

Stafford (*6*) has further commented on reclaim testing: "The co-relation of tensile strengths and the compounding value of a particular reclaim is a very vexed one, and there is a large amount of evidence and experience indicating that the two are not directly proportional." Hurleston (*1*) has also suggested testing reclaimed rubber by admixture with crude rubber together with "curatives."

Formula I

Tube reclaim	33.00
Smoked sheets	40.00
Sulfur	2.31
Diorthotolylguanidine	0.19
Medium process oil	1.00
Zinc oxide	4.00
Whiting	19.50
	100.00

Some results of tests in typical compounds using reclaims of quite different tensile strengths, as shown by reclaim-sulfur mixes, are shown in Tables IV and V. Two tube reclaims, A and B, were tested in a low-grade inner-tube compound as shown in formula I.

Table IV. Tests on Tube Reclaims in Formula I

Formula	Cure	Number of Test Strips	Tensile Strength A	Tensile Strength B	Elongation at Break A	Elongation at Break B
	Min.		Kg./sq. cm.		%	%
	(141.7° C.)					
Reclaim 100, Sulfur 5	25	4	47	142	640	660
	(146.1° C.)					
Formula I	20	3	181	184	710	715
	25	3	190	189	695	700
	30	3	184	190	670	680

Temperature of test, 27° C.

A was made by the digester process and B by the pan process, the former having about one-third the tensile strength of B in the reclaim-sulfur test. Table IV shows that the tensile strengths are comparable when either reclaim is used in formula I.

The results of the use of whole tire reclaim of quite different physical properties, as revealed by the reclaim-sulfur test, are shown in Table V. Samples of the same type of whole tire reclaim made on the same day were used. The difference in tensile strength of 15 kg. per sq. cm. represents the maximum observed in this reclaim, which is not as great as in the two tube reclaims, but is enough to cause intense argument upon occasion. The use of these reclaims in two different tread compounds, formulas II and III, shows comparable final results.

Formula II

Whole tire reclaim	25.000
Smoked sheets	42.500
Diphenylguanidine	0.375
Sulfur	1.625
Carbon black	19.500
Zinc oxide	8.000
Pine tar	3.000
	100.000

Formula III

Smoked sheets	35.0
Whole tire reclaim	35.3
Sulfur	1.8
Mercaptobenzothiazole	0.4
Stearic acid	2.0
Zinc oxide	2.5
Mineral rubber	5.0
Carbon black	18.0
	100.0

Table V. Tests on Whole Tire Reclaim in Formulas II and III

Formula	Cure	No. of Test Strips	Elongation at Break L[a]	Elongation at Break H[a]	Stress at 400 Per Cent Elongation L	Stress at 400 Per Cent Elongation H	Tensile Strength L	Tensile Strength H
	Min.		%	%	Kg./sq. cm.		Kg./sq. cm.	
			Temperature of test, 22° C.					
	(141.7° C.)							
Reclaim 100, Sulfur 5	25	8	410	350	27	47	41	56
			Temperature of test, 30° C.					
	(143.3° C.)							
Formula II	30	3	705	710	65	63	172	167
	45	3	700	690	78	84	198	200
	60	3	670	660	92	94	207	207
	75	3	645	635	96	98	208	205
	90	3	635	620	99	102	208	197
			Temperature of test, 29° C.					
	(125.7° C.)							
Formula III	30	3	695	665	83	87	192	194
	45	3	635	615	96	103	200	198
	60	3	600	610	109	107	199	200
	75	3	610	600	113	116	205	203

[a] L, whole tire reclaim, low tensile. H, whole tire reclaim, high tensile. Stress for reclaim-sulfur mixes is at 300 per cent elongation.

In compounds of the mechanical goods type, where often the reclaim is the major constituent of the compound, a definite average difference in reclaim-sulfur tensile strength may carry over to the compounds, showing a trend but not proportionally. Tests on formula IV, as recorded in Table VI, show a case where there is a small but essential difference in tensile and a definite difference in elongation in the compound. These differences are indicated in the reclaim-sulfur tests but not in the correct proportion, although the change in manufacture of the reclaim should assure the difference, as indicated by the results obtained when the reclaims are tested in formula IV.

Formula IV

Blend reclaim	70.0
Sulfur	1.6
Diphenylguanidine	0.5
Lime	3.5
Zinc oxide	1.0
Whiting	18.4
Paraffin	0.5
Medium process oil	4.5
	100.0

Table VI. Tests on Blend Reclaim in Formula IV

Formula	Cure	No. of Test Strips	Temp. of Test	Elongation at Break Reclaim X	Elongation at Break Reclaim Y	Tensile Strength Reclaim X	Tensile Strength Reclaim Y
	Min.		*° C.*	%	%	*Kg./sq. cm.*	
Reclaim 100, Sulfur 5	(141.7° C.) 25	16	19	370	390	55	65
Formula IV	(157° C.) 8	16	29	185	215	36.5	38.3

The results of tensile-elongation testing on reclaim-sulfur mixes, therefore, force certain conclusions:

1. With the best testing conditions and with sufficient tests, reproducible results may be obtained.
2. Under routine testing conditions which do not allow sufficient tests, the results are accurate at best to 10 per cent, and will many times be less accurate than this.
3. Even the best results are not a criterion of the properties of the reclaim in the recipe in which it is to be used.

Discussion

The manufacturer of reclaimed rubber must avail himself of any test which can be run in his factory or laboratory, inasmuch as he cannot have available all the typical processing equipment of his varied consumers. It is fortunate that physical tests on raw reclaim give results which indicate closely most processing conditions. The reclaim manufacturer may also run processing tests on type compounds in which the reclaim is being used, or through coöperation with the consumer he may run these tests in a specific test compound submitted by that particular consumer. In this way the manufacturer does the most he can in the way of control testing.

While the manufacturer is limited by not knowing each specific compound in which his material is used and by not having available each specific set of equipment suitable for processing tests on this type of compound, the consumer on the other hand is in the position to carry out actual tests on his own equipment and in his own compound which will give the only accurate criterion for evaluating any raw material including reclaimed rubber.

Therefore, for the examination of reclaimed rubber by the consumer the following procedure is recommended:

1. On a sample shipment, a small sample from each slab, the whole being blended, should be used. On a carload shipment current practice is generally to take six to ten samples from the car, blending these for test.
2. Chemical tests should be run for any specific constituent.
3. Specific gravity on a reclaim-sulfur mix should be obtained.
4. Laboratory processing tests on the raw reclaim and in a test recipe, also physical tests on the cured test compound, may be made. Unless these tests are known to have a direct and accurate interpretation in reference to the actual processing and tests on the finished product, they should be omitted entirely.
5. An actual factory run of one or a few mixings of a typical compound should be made, wherein actual processing is noted and tests are made on the finished product.

Any manufacturer who will follow the above practice is performing his tests on reclaimed rubber recipes in the most practical and most satisfactory manner, and the results obtained in utilizing procedure 5 above are particularly satisfying from the standpoint of both consumer and manufacturer.

For many years the reclaimer has heard his product accused of being responsible, because of variation, for many of the multitudinous ills occurring in rubber manufacturing plants. As recently as 7 years ago many of these complaints were justifiable. Because of the progressive advances in control towards uniformity of production in the past 5 to 7 years, very few complaints of any kind are justifiable today. Every reclaimer has had experiences in which his product was held culpable, only to be able to prove that another factor was the cause of the difficulty. Further, every reclaimer will appreciate knowing the facts on which a just complaint is based, since they make available to him experience and knowledge through which he may profit. Reclaimed rubber should be considered only as an important compounding ingredient, and for the benefit of both consumer and manufacturer a rational, practical, and thorough testing procedure is indispensable.

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Germany Develops Improved Process of Sterilizing Artificial Ice. A new process of sterilizing ice has been introduced in Germany, according to a report made public by the Commerce Department. Sterilized ice has up to now been produced throughout the world by freezing sterilized water, it is pointed out. This ice was always liable, however, to be infected during transfer from the factory to the user. There was, furthermore, the possibility of germs being transferred indirectly to the foodstuffs in ice-cooled rooms.

George Kaune, a Munich scientist, is reported to have succeeded in applying his Katadyn process, consisting of the sterilization of water by the use of metallic silver, to the production of artificial ice. The use of this process has resulted in obtaining totally different results. Artificial ice made from water treated with this process not only is sterile, but in addition has bactericidal qualities. For this reason, it is being designated in Germany as "activated ice" to distinguish it from ordinary artificial or natural ice.

Careful bacteriological tests, carried out at the Hygienic Institute of the Dresden Technical University are said to have proved that germs introduced into the melting water of activated ice were killed after a few hours, so that the certain destruction of any bacteria that come in immediate contact with the ice may be safely relied upon.

New Type of Antimony Electrode for pH Measurements

T. R. Ball, Webster B. Schmidt, and Karl S. Bergstresser, Washington University, St. Louis, Mo.

An investigation of the antimony–antimony oxide electrode for measuring pH was begun by Schmidt in this laboratory in the fall of 1931. The work was practically completed when the publication of Parks and Beard (*3*) appeared. Aside from the fact that these authors used a vacuum-tube potentiometer for their potential measurements, the two investigations were practically identical. Parks and Beard found that the electrode functions between a pH of 2 and 7, which is in perfect agreement with results in this laboratory. However, in calculating the pH Parks and Beard use the equation $E = -0.007 + 0.05195$ pH at 25°, while the present authors found that the equation $E = -0.020 + 0.05813$ pH at 20° gives the proper pH within about 0.02 unit when E is measured against a saturated calomel electrode with a Leeds and Northrup portable potentiometer. The difference in the value of the constant cannot be accounted for by the small difference in temperature unless the antimony electrode has a very large temperature coefficient, and probably lies in the apparatus used in making the measurements. Using 48 different electrodes prepared and annealed in various ways, very little difference was found in their performance, so that the discrepancy probably does not lie in the method of preparation or purity of the electrodes.

If it is assumed that the antimony–antimony oxide electrode functions by virtue of the changing antimony-ion activity in solutions of varying acidity, other antimony compounds should serve as a substitute for the oxide coating. The sulfide is immediately suggested. Mr. Schmidt prepared electrodes with sulfide coatings by suspending cast electrodes for 1 hour in hot 0.30 N nitric acid and then saturated the solution with hydrogen sulfide. The metal became coated with a thin yellowish film that was not removed with a stream of water from a wash bottle. These electrodes were found to function in the same manner as the ordinary antimony electrode and have the advantage of a greater range on the alkaline side. No claim is made that they are useful for precision measurements, but they will indicate the pH within ±0.05 unit in the range from 2 to 10. They are slightly better than the oxide electrodes in the rapidity of establishing equilibrium and the difference between individual electrodes is usually not more than 2 or 3 millivolts.

Time did not permit of a thorough investigation of the antimony sulfide electrode by Mr. Schmidt, but the work was carried on by Mr. Bergstresser. The data hereafter presented are taken from the work of both.

Experimental

Preparation of Electrodes. Five methods were used in preparing the sulfide coated electrodes.

1. Polished stick electrodes were immersed in 0.30 N nitric acid which was kept on the steam bath for 1 hour. The hot solution was then saturated with hydrogen sulfide while it cooled to room temperature. When not in use the electrodes were kept in this saturated hydrogen sulfide solution.
2. The procedure was identical with that of the first method, except that 0.50 N nitric acid was used.
3. Polished electrodes were placed in a long Pyrex tube which was sealed at one end and connected to a vacuum pump at the other. A small amount of sulfur was placed in the sealed end of the tube. The tube was evacuated and the portion containing the electrodes was heated to 400° C. in an electric tube furnace. In a second run a temperature of 490° C. was used. The sulfur was then distilled onto the electrodes by applying heat to the sealed end. The tube was allowed to attain room temperature before the vacuum was released.
4. Polished electrodes were heated to 400° C. in a stream of dry hydrogen sulfide.
5. A heavy coating of oxide was formed on the electrodes by heating them to 500° C. in a stream of air. The cooled electrodes were then treated with hydrogen sulfide while suspended in 0.30 N nitric acid.

A complete study of these various electrodes showed that those prepared by the first method gave more nearly reproducible results and all the data in this paper were obtained from electrodes so prepared.

Results. Table I contains typical sets of data obtained with buffers which were standardized with quinhydrone up to a pH of 7 and with a hydrogen electrode in the more alkaline range.

Table I. Calculation of Constant E_0 of Equation 1

Buffer	pH	E. M. F. vs. Sat. Cal.	t °	$E_{0_{Sb}}$	pH Calculated	pH Error
HCl-KCl	1.12	0.0540	20	(−0.2406)	1.21	+0.09
Phthalate-HCl	2.20	0.1100	20	−0.2339	2.18	−0.02
Phthalate	3.92	0.2125	24	−0.2358	3.93	+0.01
Phthalate	3.97	0.2135	20	−0.2345	3.96	−0.01
Phosphate	5.29	0.2930	20	−0.2377	5.33	+0.04
Phosphate	5.54	0.3074	24	−0.2353	5.54	±0.00
Phosphate	5.91	0.2370	20	−0.2355	5.92	+0.01
Phosphate	6.66	0.3739	24	−0.2358	6.67	+0.01
Phosphate	6.97	0.3870	20	−0.2337	6.95	−0.02
Borate	8.01	0.4480	20	−0.2347	8.00	−0.01
Borate	9.20	0.5160	20	−0.2331	9.17	−0.03
Phosphate	10.00	0.5615	20	−0.2324	9.96	−0.04
			Av.	−0.2348		
Phosphate	10.28	0.5935	23	−0.2437	10.43	+0.15
Phosphate	10.82	0.5966	22	−0.2166	10.51	−0.21
Phosphate	11.41	0.6438	23	−0.2472	11.60	+0.19
Phosphate	11.77	0.6714	22	−0.2359	11.79	+0.02
Phosphate	12.11	0.7046	23	−0.2473	12.40	+0.19

The e. m. f. values of column 3 are the averages obtained from four or more electrodes measured against the saturated calomel electrode. The E_0 values of column 5 are calculated from the equation

$$E_0 = \text{pH}\,[0.0577 + 0.0002\,(t - 18)] - \text{e. m. f.} - E_{\text{cal.}} \qquad (1)$$

The value of $E_{\text{cal.}}$ at any given temperature was computed from the equation (*2*)

$$E_{\text{sat. cal.}} = 0.2504 + 0.00065\,(t - 18) \qquad (2)$$

The average value of E_0 is computed over the pH range of 2.2 to 10 only, since in the more acid and alkaline ranges the electrodes behave erratically. Having established the value of the constant E_0 as −0.2348 volt, the pH of each solution was calculated to the closest 0.01 unit from Equation 3.

$$\text{pH} = \frac{\text{E. m. f.} + E_{\text{cal.}} - 0.2348}{0.0577\,(t - 18)} \qquad (3)$$

This equation would, of course, apply to any type of calomel electrode. The last two columns show the calculated pH and the deviation from the correct value of column two. Over the range of 2.2 to 10 the pH may be relied upon to about 0.05 unit. Individual electrodes rarely differed from others in the same solution by more than 2 or 3 millivolts if the pH was 10 or less. This is somewhat better than the oxide electrodes of Parks and Beard (*3*). A study of their data shows a variation between electrodes of from 3.2 to 5.2 millivolts, even in the

most favorable range. In solutions of pH above 10, the sulfide electrodes showed a maximum variation among themselves of 11.5 millivolts. Table I shows that the sulfide electrode is not reliable in this range even when average values of several electrodes are taken.

Sugar, starch, and nitrates have no deleterious effect upon the electrodes between pH 2.2 and 10. However, hydroxy acids, such as tartaric, citric, and lactic, render the electrode useless. This has been found to be true of the antimony oxide electrode as well (*1*). The sulfide electrodes were used in the back-titration of alcoholic potassium hydroxide in determining the saponification number of oils. As would be expected, the strongly alkaline solution quickly removes the sulfide film, but the electrode still functions. The end point as determined by finding the maximum value of $\Delta E/\Delta V$ agrees with the phenolphthalein end point. In this respect the sulfide electrode offers no advantage over the ordinary antimony–antimony oxide electrode.

Summary

1. Antimony electrodes coated with antimony sulfide have been prepared by five different methods.

2. Electrodes prepared by suspension in hot 0.30 *N* nitric acid for 1 hour, followed by saturation with hydrogen sulfide, may be used to determine the pH of solutions in the range from 2 to 10.

3. Electrodes so prepared agree among themselves within about 3 millivolts if the pH is 10 or less, but may differ by as much as 11.5 millivolts in more alkaline solutions.

4. Starch, sugar, and nitrates have no deleterious effect in the range over which the electrode functions in their absence.

5. The electrode, like the oxide electrode, is useless in the presence of hydroxy acids.

6. The electrode should be useful in determining the saponification of highly colored oils, but offers no advantage over the ordinary antimony electrode.

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Colorimetric Determination of Fluorine

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THE fluoride content of natural water has taken on new significance, since the researches of Smith, Lantz, and Smith (*4*), Churchill (*2*), and Kehr (*3*) have shown that it may be the cause of the tooth defect known as mottled enamel. Of the numerous methods which have been devised for the detection and determination of fluorides, few find satisfactory application in the field of water analysis, where a very sensitive method is required.

In the modified Casares-DeBoer method used by Thompson and Taylor (*5*), the fluorides are determined by the degree of fading of a zirconium-alizarin lake. Willard and Winter (*6*) suggest the use of quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone) as an indicator in their method. Quinalizarin seems to the writers to have advantages over alizarin when used as in the Casares-DeBoer method, in that it is more sensitive to small changes in fluoride content and the change in color is easier to distinguish. For example, a difference in color between samples containing 0.2 and 0.4 part per million is greater in the case of zirconium-quinalizarin than zirconium-alizarin reagent. The best range of the colorimetric standards is from 0 to 2 p. p. m. or 0.0 to 0.1 mg. of fluoride per 50 ml. Above this concentration the fading is too great, and comparisons are not easily made.

Recommended Method

The zirconium-quinalizarin reagent is prepared by mixing equal parts of a 0.14 per cent solution of quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone) and an 0.87 per cent solution of zirconium nitrate, and diluting the mixture 1 to 40. The quinalizarin is dissolved in a 0.30 per cent sodium hydroxide solution, as it is insoluble in water.

Method of Analysis. Precipitate the sulfates by the addition of 5 ml. of 2 per cent barium chloride solution to 100 ml. of the sample. After settling several hours, draw off a 50-ml. portion for the test. The barium sulfate may be filtered off if desired. Add 3 ml. of 1 to 1 hydrochloric acid and 5 ml. of the zirconium nitrate–quinalizarin reagent and mix thoroughly. After 20 minutes compare with standards made at the same time and in the same manner. Comparisons are easily made in American Public Health Association tubes with standard fluoride solution containing from 0 to 2 p. p. m. in steps of 0.2 part.

The fading of the color of the zirconium-quinalizarin or zirconium-alizarin lake is a function of time, temperature, and acidity. After 15 minutes at room temperature the change is very slow and the color remains sufficiently constant for comparisons. Care must be taken that exact amounts of indicator (zirconium-quinalizarin reagent) and acid are added to the sample and to the standards and that the time of fading is the same for unknown and standard.

Of the commonly occurring ions, none in the quantities occurring in natural or treated water affect the results except aluminum, iron, sulfates, and phosphates. Less than 20 p. p. m. of sulfates have no effect and may easily be removed by barium chloride, since the Ba^{++} ion has no effect. Iron above 10 p. p. m. changes the color, making comparisons impossible. Aluminum has no effect up to 0.2 p. p. m. as Al; above this amount and up to 0.6 p. p. m. as Al the results will be low by 0.1 p. p. m. of fluorine. Aluminum is rarely present in water in amounts greater than 1 p. p. m. expressed as Al_2O_3 or 0.5 p. p. m. as Al, and may thereby be neglected in most cases. This is further confirmed in the comparative results between those obtained by direct colorimetric and distillation methods. Phosphates affect the color when from 0.3 to 0.4 p. p. m. or more are present. The color is different and is easily recognized by one experienced in the determination. Fortunately these two substances rarely occur in water in amounts greater than 0.5 p. p. m. except in certain localities. When they do occur the distillation method seems to be the reliable procedure.

In case phosphates and aluminum are present, distillation with perchloric acid as recommended by Boruff and Abbott (*1*) will be necessary.

Place the sample containing approximately 0.2 ml. of fluoride in a 125-ml. distilling flask, and add a few glass beads and sufficient dilute sodium hydroxide to make it just alkaline to litmus. Reduce the volume to 10 to 15 ml. by distilling off the water, and obtain a 50-cc. distillate according to the procedure outlined by Boruff and Abbott (*1*).

In carrying out the distillation, care must be exercised to avoid bumping, as the presence of much perchloric acid in the distillate will seriously interfere with the colorimetric test. Its presence can be readily detected by the off color of the sample when the reagents are added. The temperature should not be allowed to rise above 150° C., in order to avoid decomposition of the perchloric acid. Sulfuric acid cannot be used, as sufficient passes over into the distillate to affect the color developed on adding the quinalizarin reagent. In routine water analysis the distillation method is time-consuming and it becomes desirable to determine how necessary is this precaution.

In a study of 201 Oklahoma waters, 177 samples had a fluoride content of 1 or less. Of these, 59 gave the same value when determined by both methods; in 88 samples the results obtained by the direct colorimetric method were below those obtained by distillation by an average of 0.13 p. p. m. of fluorine, and in 30 cases they were above by an average of 0.11 p. p. m. The 15 samples containing 1.1 to 2.0 p. p. m. and 9 containing 2.1 and above were too few in number to draw definite conclusions. These 201 cases indicate that the direct colorimetric method may give results which are about 10 per cent lower than that obtained by distillation.

The authors' experience confirms that of previous investigators that fluorine is usually found in natural waters in quantities less than 2 p. p. m., 95 per cent of the samples containing less than 2.0 p. p. m.; hence a method that is accurate to within 10 per cent of the numerical value, when the fluoride content is from 1 to 2 p. p. m., and that is rapid and reliable should be a valuable acquisition to water analysis and worthy of trial by other investigators.

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Determination of Potash in Fertilizers

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Much work has been done by the Association of Official Agricultural Chemists to overcome the inaccuracies in the present method, which specifies the determination of only the water-soluble potash, but no attempt has been made to determine the available potash, as in the case of other fertilizer constituents. This method has been in use for a long time and is incorporated in practically all state laws, but there is no logical reason why it should be continued if it does not show the correct results in available potash.

A series of tests was made on a number of mixed fertilizers, including the five samples sent out by the Chemical Control Committee of the National Fertilizer Association, to determine the effect on the percentage of potash produced by washing with larger quantities of water than are specified by the official method. Four successive leachings were made on each sample with approximately 225 cc. of water, and the potash was determined in the separate solutions and in the final residue. Potash was also determined in solutions made with 1 per cent hydrochloric acid. Blank tests were made on all reagents, and the same method was employed in all analyses. The results are shown in Table I.

Table I. Potash Determinations in Solutions from Successive Leachings with Water, from Residue, and from Hydrochloric Acid Solutions

Sample	Leachings[a] First	Second	Third	Fourth	In Residue	Total	Boiled 1 Per Cent HCl Solution
1	17.24	0.10	0.04	0.02	0.16	17.56	17.50
2	3.90	0.11	0.04	0.02	0.40	4.47	4.40
3	3.88	0.12	0.05	0.02	0.40	4.47	4.20
4	4.04	0.07	0.03	0.03	0.07	4.24	4.22
5	3.96	0.10	0.02	0.02	0.04	4.14	4.17
6	5.32	0.06	0.05	0.04	0.09	5.56	5.65
7	4.18	0.04	0.05	0.03	0.14	4.44	4.48
8	3.10	0.03	0.04	0.03	0.17	3.37	3.27
9	3.92	0.09	0.05	0.03	0.13	4.22	4.24
10	5.38	0.10	0.05	0.03	0.13	5.69	5.66
11	6.15	0.02	0.02	0.01	0.14	6.34	6.36

[a] 225 cc. each.

These analyses show that potash is being recovered in small amounts in the fourth washing, after approximately 900 cc. of water have passed through the material, and there still remains from 0.04 to 0.40 per cent in the residues. If the washings had been continued, it is probable that most of the potash would finally have been recovered. If the sum of potash obtained in the different leachings, plus that in the residues, is compared with that obtained in the acid solutions, the results are in close agreement.

The two samples showing the largest amount in the residue, 0.40 per cent, were also tested by washing with water and digesting in ammonium citrate, as in the determination of insoluble phosphoric acid. The results showed 0.06 per cent of insoluble potash in each case.

Solutions made with 1 per cent hydrochloric acid give very good results, especially if neutralized with caustic soda instead of ammonia. There should be no objection to this procedure, as insoluble silicates are not decomposed in acid solutions of this strength.

In all samples the potash was supplied from a soluble source, and the results indicated that some of the potash is slightly fixed, so as to yield slowly to solution in water, but is in a form which is assumed to be readily available as a plant food. This is supported by the fact that the insoluble portion is soluble in ammonium citrate, the standard test for available phosphoric acid. As these tests were made on regular grades of mixed fertilizers, no data are available concerning the amount of potash in the different components, but in previous work similar losses have been confirmed on carefully formulated theoretical mixtures.

Conclusion

Much work has been done to perfect the official method so as to obtain theoretical results, but it would appear that the only remedy for correcting the inaccuracies is to change the method so as to determine available instead of water-soluble potash.

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Use of Aëration in Kjeldahl Distillations

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THE extremely useful method for the determination of nitrogen in organic substances, brought forward by Kjeldahl in 1883 (*5*) as an extension of a method first applied to urea in 1875 by Heintz and Ragsby (*4*), has undergone a number of modifications to widen the scope of its application and to facilitate the analysis. One has been the aëration of the alkalized solution to expedite the sweeping over of the ammonia into the standard acid solution. Suggested by Folin in 1903 (*3*) in connection with urine analysis,

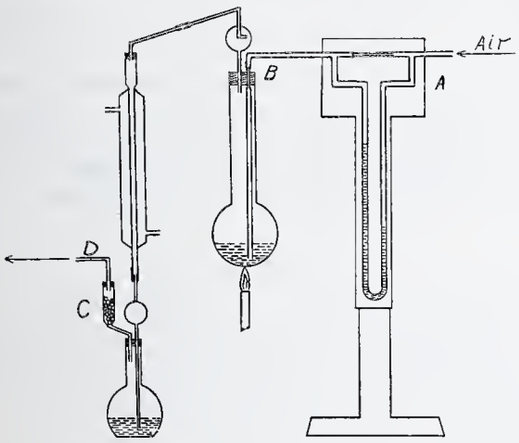

Figure 1. Diagram of Apparatus

it was proposed as a general procedure in Kjeldahl distillations by Kober in 1908 (*6*) and by Sebelien in 1909 (*7*). Dillingham in 1914 (*1*) and Falk and Sugiura in 1916 (*2*) demonstrated that complete recovery of the nitrogen by aëration alone was not practicable but that heat was also necessary; aëration alone, even when carried on for several hours, resulted in the recovery of less than 95 per cent of the nitrogen.

Although aëration with simultaneous heating has been used by many analysts with satisfactory results, no critical examination of the method seems to have been made. The authors of this paper failed to find any data in the literature on nitrogen recovery under various experimental conditions or any information as to the most desirable procedure. Accordingly a critical examination was carried through, some of the results of which are summarized in this communication.

Procedure

The substance selected for analysis was *N*-butyramide, procured from the Eastman Kodak Co., and found to give satisfactorily reproducible analyses from a large batch in close agreement with the theoretical nitrogen content of 16.09 per cent. A sample of about 0.2 gram was oxidized with 40 grams of concentrated sulfuric acid, to which were added 10 grams potassium sulfate and 0.5 gram of mercury. The digestion was continued for 30 minutes after the contents of the Kjeldahl flask became colorless.

The ammonia distillation was carried out using the apparatus shown in Figure 1. By the application of suction at *D*, air from outside the laboratory was drawn in through the flowmeter *A* and the inlet tube *B*, passed over together with steam and ammonia, bubbled through the standard acid solution, and drawn out through the guard tube *C*. The guard tube *C* contained glass beads without perforations, and through it the acid solution and the methyl orange indicator were introduced into the receiving flask. The beads, remaining wet with the colored acid solution, served to show whether or not the ammonia was being completely absorbed and to absorb any such that came through; change to the alkaline color at the base of the tube usually did occur, more markedly in the case of high aëration rates. The sodium sulfide solution to precipitate the mercury and the excess sodium hydroxide solution were admitted through a funnel temporarily attached to the inlet tube, *B*. The temperature of distillation was read from a thermometer attached to the inlet tube inside the flask. To this temperature the solution was raised as rapidly as practicable before aëration was begun.

The effects of varying the conditions upon which the rate of distillation might depend were in turn examined. The more important conclusions so far as this investigation was concerned are brought out by the data given in Tables I and II and plotted in Figures 2 and 3.

Table I. Nitrogen Recovery for Various Aëration Rates at Various Temperatures

Temperature	Aëration Rate	Nitrogen Recovered	Per Cent Recovery
° C.	L./min.	%	
25	0.2	0.36	2.24
	0.4	0.54	3.36
	0.6	0.64	3.98
	0.8	1.00	6.22
50	0.2	0.62	3.85
	0.4	1.28	7.96
	0.6	1.63	10.13
	0.8	1.87	11.62
75	0.2	1.91	11.88
	0.4	3.74	23.24
	0.6	5.40	33.56
	0.8	7.01	43.57
90	0.2	6.05	37.60
	0.4	9.21	57.21
	0.6	11.21	69.67
	0.8	12.33	76.63
100	0.2	13.56	84.27
	0.4	15.26	94.84
	0.6	16.00	99.44
	0.8	16.06	99.81

Data obtained using a sample of 0.2 gram, a total volume for distillation of 250 ml., and with 20-minute distillation. Complete recovery equals 16.09 per cent nitrogen.

It was found that increasing the dilution of the solution greatly slowed up the rate of ammonia distillation. With a solution temperature of 90° C. and an aëration rate of 0.8 liter per minute, the recovery for 15 minutes' distillation

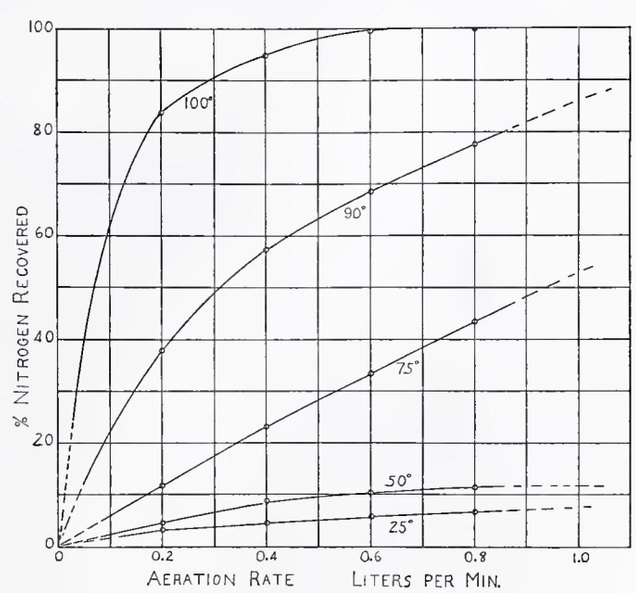

Figure 2. Relation of Nitrogen Recovery to Aëration Rate

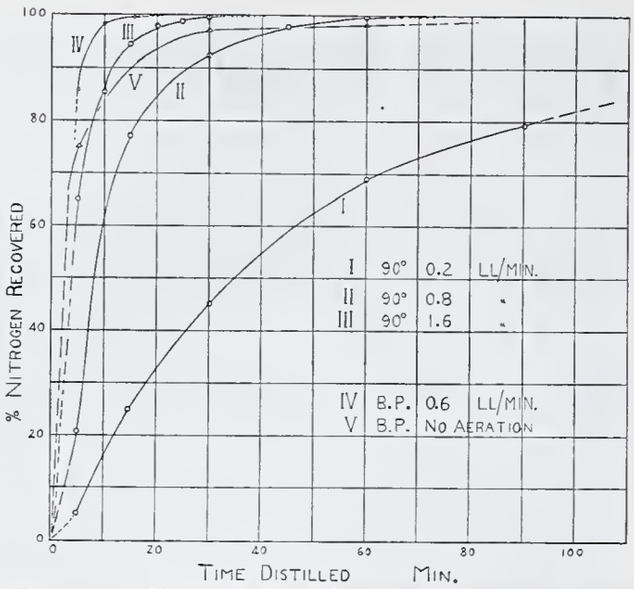

Figure 3. Variation of Nitrogen Recovery with Time of Distillation

was 95.93, 79.86, and 58.67 per cent, from total volumes of 100, 300, and 500 ml., respectively.

It was also found that it makes little difference whether the inlet tube delivers the air in large bubbles or in small bubbles distributed more widely through the solution.

Summary

1. The conditions favorable for carrying out Kjeldahl distillation using aëration are indicated. With fairly rapid aëration at the boiling point of the solution distillation is complete in less than 15 minutes.

2. In addition to the saving of time involved, the use of aëration is recommended because of the entire absence of bumping and the obviation of the danger of acid solution backing up into the condenser. The apparent disadvantage of more complex apparatus is actually very slight, the only additional requisites to that needed for an ordinary distillation being the guard tube and inlet tube, neither of which requires more than rinsing between distillations.

Table II. Nitrogen Recovery for Various Times of Distillation

Aëration Rate	Time of Distillation	Nitrogen Recovered	Per Cent Recovery
L./min.	*Min.*	%	
0.2	5	0.95	5.90
	15	3.93	24.42
	30	7.20	44.74
	60	11.08	68.89
	90	12.78	79.43
0.8	5	3.41	21.19
	15	12.32	76.57
	30	14.89	92.54
	45	15.59	96.88
	60	16.11	100
1.6	5	10.51	65.32
	10	13.72	85.27
	15	15.27	94.94
	20	15.75	97.89
	25	15.95	99.12
	30	16.10	100

Data obtained using a sample of 0.2 gram, a total volume of solution of 250 ml., and a distillation temperature of 90° C. Complete recovery equals 16.09 per cent nitrogen.

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Determination of Lead as Dilead Hydrogen Arsenate

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An investigation in this laboratory (*2*) on the system PbO–As_2O_5–H_2O showed that dilead hydrogen arsenate, $PbHAsO_4$, is very insoluble; the results indicated that its solubility is comparable to that of the chromate and sulfate. Since this compound exists over such a wide range of acidity, the suggestion was made that lead might be determined quantitatively by precipitation as the dilead hydrogen arsenate.

The aim of this paper is to present in very brief form the results of an attempt to devise a quantitative method for the determination of lead in commercial lead arsenate. The method is not so adaptable as the chromate and sulfate methods for easy control and consequently it is not necessary to give in detail the experimental results (*1*).

Preliminary experiments made on the precipitation of lead as dilead hydrogen arsenate, by adding disodium arsenate solution to a standard solution of lead nitrate, showed that the acidity of the solution had a marked influence on the composition of the precipitate.

A series of determinations was next carried out using disodium hydrogen arsenate–arsenic acid buffer solutions of varying pH. Precipitation was accomplished by adding a definite quantity of the lead nitrate solution to varying amounts of the arsenate buffers. All precipitates were collected and washed on asbestos pads in Gooch crucibles and dried at 120° C. The pH of the solutions changed considerably during the precipitations, becoming more acid. The data afforded evidence that a still greater control of the hydrogen-ion concentration would be necessary to obtain precipitates corresponding in composition to dilead hydrogen arsenate.

Further experiments showed that lead can be precipitated quantitatively from a solution of lead nitrate as dilead hydrogen arsenate by the use of a disodium hydrogen arsenate–arsenic acid buffer solution. The proper acidity necessary for precipitation is pH 4.6—that is, just alkaline to methyl orange. Any marked change in the acidity due to the liberation of nitric acid will materially change the composition of the precipitate obtained. The acidity can be kept sufficiently constant during the precipitation by the gradual addition of a dilute solution of sodium hydroxide using methyl orange indicator. The arsenate solution should be subjected to mechanical stirring during the precipitation.

Attempts were also made to precipitate as dilead hydrogen arsenate the lead in samples of commercial lead arsenate. The samples were dissolved in 0.5 *N* nitric acid. The results indicated that fairly accurate results can be obtained. The procedure is laborious and necessitates too close control to rival the present accurate sulfate and chromate methods.

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Purification of Substances by Electrodialysis

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MANY references are to be found on the subject of electrodialysis, and new applications and uses are numerous. Most of the data reported in the present paper have resulted from research necessary to obtain a substance of a certain purity for use in some other investigation.

The apparatus used in the electrodialysis experiments was essentially that described by Holmes and Elder (*4*). In all experiments a piece of platinum foil was placed between the carbon anode and the filter paper. Parchment and Cellophane membranes were used throughout the investigation.

Electrodialysis of Casein

Samples of both acid and rennin casein were obtained from the research laboratory of the Borden Company. The ash content of acid casein before electrodialysis was 3.69 per cent and after 56 hours of electrodialysis was 0.067 per cent, a 98.4 per cent removal of ash. The acid casein (8.41 grams) was suspended in dilute acetic acid and diluted to 850 cc. Ammeter readings varied from 0.22 ampere at the start to 0.027 ampere at the end. The maximum and minimum temperatures within the cell were 45° and 25° C., respectively. A sliding resistance was used to keep the cell from heating too much. During electrodialysis a horny material deposited on the cathode membrane, and, when dried, had an ash content of 0.069 per cent.

In two other electrodialysis experiments no acetic acid was added, but the acid casein was kept in suspension by vigorous mechanical stirring. Ash removals of 95.2 and 97.3 per cent were obtained after 42.2 and 28 hours, respectively. In the first of these two runs the ammeter readings were 0.130 maximum and 0.0091 minimum, and in the second 0.425 and 0.0108. Temperature variations were from 25° to 51° C. Of the 11.35-gram sample of acid casein used in the second run, 8.81 grams were recovered by filtering the electrodialyzed solution.

Removal of the ash from rennin casein was not as satisfactory. The original ash content was 7.98 per cent and the final 2.17 per cent, an average ash removal of 72.9 per cent. Considerable difficulty was encountered with casein sticking to the mechanical stirrer.

Electrodialysis of Grape Juice

It appeared likely that the ash content of unfermented grape juice could be lowered by electrodialyzing out the tartrates present. Cellophane membranes were mounted wet on the cell and held in place by rubber bands. The potential current was held at 120 volts. The drip water was collected through funnels supported below the filter papers which were between the carbon blocks and the Cellophane membranes.

In preliminary experiments Kahlbaum's c. p. potassium acid tartrate was added to water and electrodialyzed, using Sutton's method (*6*) to determine the tartaric acid in the positive drip. Ninety-six per cent of the potassium acid tartrate was recovered in the drip waters and in the cell; 40 per cent of the 4.08-gram sample placed in the electrodialysis cell was removed in 12 hours by electrodialysis. As a further check on the acid collected in the positive drip, carbon and hydrogen analyses were made, and the excellent checks obtained indicated that nearly pure tartaric acid was obtained in the positive drip water.

Samples of commercial grape juice were diluted 1 to 1 and placed in the electrodialysis cell. The average of several determinations gave 18 to 20 per cent removal of the tartrate radical present in the grape juice in 3 hours. The flavor of the grape juice was unchanged by electrodialysis. The main pigments, anthocyanins or enins (*1*, *2*), in grape juice did not come through the membranes during the electrodialysis.

Electrodialysis of Sugars

One difficulty encountered by workers in sugar chemistry is that of preparing the sugar in an ash-free condition. The isolation and purification of arabogalactan by the lead-tannate method of Schorger and Smith (*5*) result in a product which even under very careful purification contains an appreciable amount of ash, only a portion of which under normal conditions is removable by repeated solution and precipitation.

This procedure results in a great loss of the purified sugar. The ash content of material purified by such methods is never so low that the sugar may be considered ash-free. Englis and others (*3*) found that electrodialysis of samples of artichoke sirup, from which levulose is obtained, produced part of the necessary acidification which resulted in a final lower ash content of the levulose. They found that the colloid content of the extract was also reduced.

Table I shows typical results in further purification of sugars by electrodialysis. The amorphous powder, sample III, before electrodialysis was straw-colored and had an ash content of 1.39 per cent. After electrodialysis and subsequent precipitation the sugar was snow-white and contained 0.063 per cent of ash. Aqueous solutions before electrodialysis were slightly turbid, while the dialyzed solutions were perfectly clear, making possible accurate polariscopic readings. The reducing value of the sugar was unchanged by electrodialysis, indicating that no hydrolysis took place during the purification. The maximum temperature during the electrodialysis was 55° C.

Table I. Purification of Sugars by Electrodialysis

	Sample I	Sample II	Sample III
Sugar	Galactose	Arabo-galactan	Arabo-galactan
Volts	120	120	120
Maximum and minimum ammeter readings	0.0128–0.004	0.05–0.0129	0.2–0.006
Maximum temperature	46° C.	26° C.	55° C.
Period of electrodialysis (hours)	48	43	72
Weight of sugar at start (grams)	7.6	10.31	10
Weight of sugar recovered (grams)	5.02	9.0	7.64
Ash content at start (per cent)	0.156	0.278	1.39
Ash content purified product (per cent)	0.0135	0.027	0.063
Ash removal (per cent)	91.3	90.3	95.6
Specific rotation	Unchanged	Not taken	Unchanged

The material of sample III was prepared from Western American larch wood by the original method of Schorger and Smith (*5*), whereas that in sample II was isolated by the method of Wise and Peterson (*7*), which accounts for the difference in ash content. Reprecipitation of the sugar from samples II and III by the use of 95 per cent ethyl alcohol gave a product which settled very rapidly and left a clear supernatant mother liquor. The galactose, sample I, was a product of the Pfanstiehl Products Company.

Further studies are being made on other simple sugars, polysaccharides, and hemicelluloses.

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New Apparatus for Determination of Size Distribution of Particles in Fine Powders

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EVERY year a greater need for accurate analysis of the size distribution of subsieve material is being felt by the engineer, because of the increasingly vital part it plays in the manufacture of cement, pigments, and other powdered products. Sieves are a satisfactory means of obtaining this information as long as the material is relatively coarse, but when from 70 to 95 per cent of the sample passes the 200-mesh screen (the finest one giving consistent reading), some new scheme of analysis must be used.

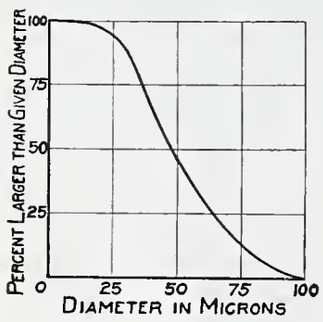


FIGURE 1. CUMULATIVE DISTRIBUTION CURVE

Several methods of analyzing this fine fraction have been developed. For example, Professor Work at Columbia has perfected an excellent microscope technic. Elutriation and sedimentation methods employing various fluid media have been shown to be feasible, and additional methods are constantly being developed, but most of them are slow and tedious.

Some time ago the Riverside Cement Company inaugurated a comprehensive research program. A consideration of its scope quickly showed that to carry on the program it was absolutely necessary to have some reliable method of making large numbers of subsieve analyses. After considerable study it was concluded that none of the existing instruments were satisfactory for the purpose; therefore, the development about to be described was undertaken.

Before starting the design of the instrument a careful analysis of the needs of the research program was made, which resulted in setting up the following five specifications:

1. High accuracy.
2. Ability to determine complete size distribution as distinguished from a fineness modulus or a value of total surface.
3. Capacity for analyzing a large number of samples per day.
4. Ability to use relatively large samples to reduce sampling errors.
5. Freedom from personal equation of the operator.

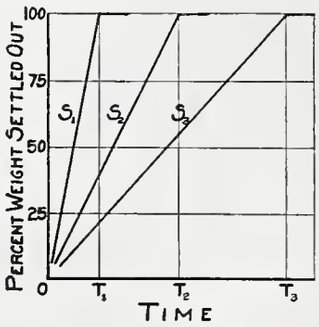


FIGURE 2. SETTLING CURVE

The principle upon which the new instrument was to operate was then chosen by comparing the above specifications with the operating characteristics of existing instruments.

The microscopic method was eliminated because it was too slow and employed too small a sample. Elutriators appeared unsuitable because of their doubtful accuracy and the length of time required to separate the sample into a large number of fractions. Methods involving light-scattering appeared to show promise for the determination of total surface but not for size distribution. In spite of the fact that existing instruments required prohibitive amounts of attention and their results were largely qualitative, the sedimentation method appeared to be the most promising; consequently this principle was adopted as the basis of the new design.

THEORY

STOKES' LAW. When a small body is allowed to fall freely in a viscous field, it soon reaches a velocity where the downward acceleration is balanced by the friction. Therefore, the velocity ceases to increase. This limiting velocity is expressed by the equation known as Stokes' law

$$V = \frac{2g(\sigma - \sigma_m)r^2}{9\eta} \tag{1}$$

where V = velocity of fall
g = acceleration of gravity
σ = density of falling substance
σ_m = density of fluid medium
η = viscosity of fluid medium
r = radius of the particle

For the present purpose, the time required for a particle to fall a given distance is more interesting than the velocity. Therefore, the equation becomes

$$T = \frac{H}{V} = \frac{9H\eta}{2g(\sigma - \sigma_m)r^2} \tag{2}$$

where T = time of fall
H = height of fall

If the height, viscosity, and densities are held constant, this becomes

$$T = \frac{K}{r^2} \text{ or } r = \frac{K_1}{\sqrt{T}} \tag{3}$$

K and K_1 being constants.

If a known weight of material composed of different sized particles is allowed to settle a distance H through a column of liquid, the relation between the weight of the material reaching the bottom and the time can be determined. By means of Equation 3, values of the radius, r, or diameter, d, can be substituted for the corresponding times, T, and the curve similar to Figure 1 constructed.

This curve supplies the desired information about the size distribution of the particles in the sample. Unfortunately,

there are great difficulties in the experimental determination of this curve. The most serious one is encountered when an attempt is made to start a sample settling from the top of the column of liquid. Since the layer of sample (dry or mixed with a small quantity of liquid) is considerably more dense than the underlying liquid, the condition is very unstable and the sample tends to go en masse to the bottom, forming strong eddy currents on the way. This is a fundamental difficulty, and one for which as yet no remedy has been found.

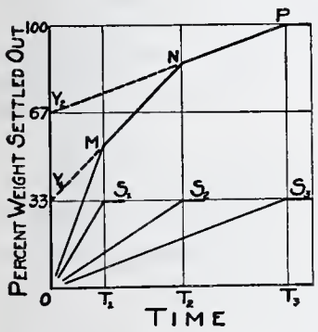
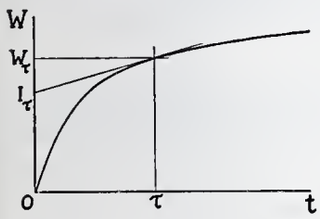


FIGURE 3. SETTLING CURVE

OPERATION OF SEDIMENTATION APPARATUS (*3*). The simplest method of starting sedimentation is to stir the sample thoroughly into the liquid until a homogeneous mixture is obtained, and then allow it to settle. However, this entirely changes the relation between the time of settling and the amount of material reaching the bottom, because the height is no longer the same for each particle. Nevertheless, there is a definite relation between the rate of settling in this latter case and that of the hypothetical sample which is all started from one definite height. Therefore, if the time settling rate relation is determined for the homogeneous mixture, the size distribution of the particles in the sample is readily obtainable. This relation is unique and interesting and is best illustrated by the consideration of a hypothetical example.

A sedimentation column of height H is available. Three samples of known uniform size are to be used: The first sample, s_1, consists of particles, all of which have a radius r_1; the second, s_2, of radius r_2; and the third, s_3, of radius r_3. All the constants of Equations 2 and 3 are known. Substituting in the numerical values, it is determined that the particles of s_1 will settle distance H in T_1 minutes, s_2 in T_2, and s_3 in T.



First s_1 is placed in the sedimentation column, mixed thoroughly, and allowed to settle. Since the particles are all of the same size, they will all settle with the same velocity. As they are distributed uniformly throughout the column, the amount collected on the bottom will be a linear function of the time, being 0 per cent at time 0, and 100 per cent at the time T, as shown in Figure 2, curve s_1. Likewise, if sample s_2 is tested in the same manner the result will be represented by curve s_2, and in the same way s_3 is obtained. All these relations are straight lines, because all the samples consisted of uniform sized particles, which were uniformly distributed in the sedimentation chamber.

Now, a sample consisting of one-third s_1, one-third s_2, and one-third s_3 is placed in the sedimentation column. If s_1 were settling out alone it is obvious that the curve would be the one labeled s_1 in Figure 3, since there is only $33^1/_3$ per cent of s_1. Likewise s_2 and s_3 would be as shown, if either were the only one present.

Since they are all settling together, in the time T_1, all of s_1 will be out, together with a per cent of s_2 and b per cent of s_3; therefore, the total per cent out will be:

$$M = 33^1/_3 + a + b$$

but

$$a = 33^1/_3 \times \frac{T_1}{T_2} \text{ and } b = 33^1/_3 \times \frac{T_1}{T_3}$$

Therefore

$$M = 33^1/_3 \left(1 + \frac{T_1}{T_2} + \frac{T_1}{T_3}\right)$$

Likewise at time T_2 all of s_1 and s_2 will be out, together with

$$c = 33^1/_3 T_2/T_3 \text{ from } s_3$$

That is,

$$N = 33^1/_3(1 + 1 + T_2/T_3)$$

At time T_3, all the sample will have settled out, so point P = 100 per cent. Since the individual settling curves are straight lines, the composite curve will be the broken straight line *O-M-N-P*. It is instructive to investigate where *N-M* produced crosses the y axis—i. e. the point Y_1. By inspection this simple geometric relation is obtained:

$$Y_1 = M - T_1 \left(\frac{N - M}{T_2 - T_1}\right)$$

Substituting in the previously determined values for M and N and simplifying, this becomes $Y_1 = 33^1/_3$.

Likewise, $P - N$ produced intersect the y axis at Y_2

$$Y_2 = N - T_2 \left(\frac{P - N}{T_3 - T_2}\right)$$
$$= 66^2/_3$$

This is significant, since $33^1/_3$ is the per cent of s_1 in the total sample, and $66^2/_3$ is the sum of the percentages of s_1 and s_2.

ODEN'S INTERPRETATION OF SETTLING CURVES. The above hypothetical example serves to illustrate the method used by Oden to interpret settling curves. He proved that the above relations hold in any suspension of different sized particles of the same substance where the sizes are such that they follow Stokes' law. A general statement of the method is as follows:

If the sedimentation curve is plotted with the time of the settling as abscissa and the weight of the material as ordinate, then the intercept on the y axis of a tangent to the curve at a point T will give the per cent of the sample whose particles have diameters equal to or larger than that of a particle which would just settle a distance equal to the height of the sedimentation column in the time T.

A more mathematical derivation of this relation is given below.

PROOF OF INTERCEPT METHOD OF INTERPRETING SETTLING CURVES. The derivation postulates (*a*) that particles of a given diameter have a constant and characteristic rate of fall in a given liquid; (*b*) that the particles are uniformly distributed throughout the liquid at the instant settling commences; and (*c*) that the particle concentration is sufficiently low so that there is no interference.

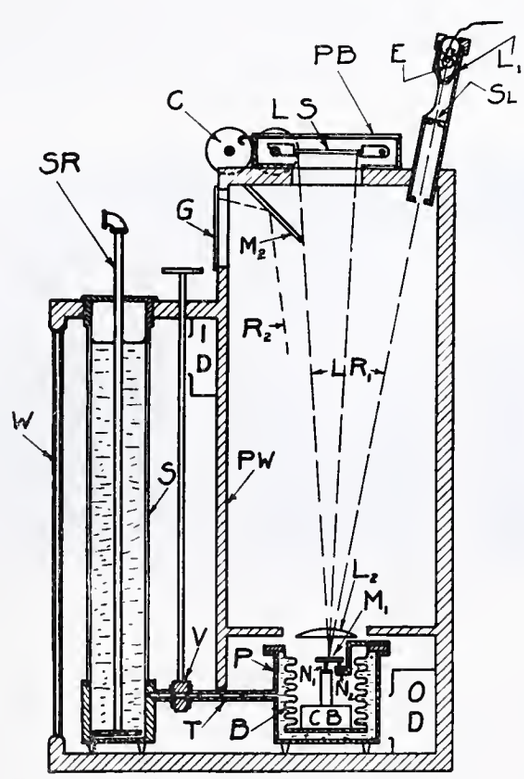


FIGURE 4. SECTIONAL DIAGRAM OF MICRONETER UNIT

Given a settling curve of weight settled out, W, plotted as a function of time t, let W_t equal the weight of the fraction whose particles have a fall time t for the height of the liquid column.

Therefore $\frac{W_t}{t}$ equals the rate of settling out of this fraction and $\tau\frac{W_t}{t}$ equals the weight of this fraction settled out in time τ.

Now $\frac{dW}{dt} = \int_t^\infty \frac{W_t}{t}dt$, since all fractions with settling times of t or less are all settled out and therefore do not contribute to $\frac{dW}{dt}$.

Consider time τ:

$$W_\tau = \int^\tau W_t dt + \int_\tau^\infty \tau\frac{W_t}{t}dt$$

$$= \int_0^\tau W_t dt + \tau\int_\tau^\infty \frac{W_t}{t}dt \qquad (4)$$

That is, total weight settled out at time τ = the sum of all fractions having settling times of τ or less + proportional amounts of all fractions having settling times greater than τ.

Now

$$\left[\frac{dW}{dt}\right]_\tau = \int_\tau^\infty \frac{W_t}{t}dt \qquad (5)$$

Substituting in Equation 4

$$W_\tau = \int_0^\tau W_t dt + \tau\left[\frac{dW}{dt}\right]_\tau$$

or

$$\int_0^\tau W_t dt = W_\tau - \tau\left[\frac{dW}{dt}\right]_\tau$$

$$= I_\tau \qquad (6)$$

since $\int_0^\tau W_t dt$ is the total weight of all fractions having settling times of τ or less.

It should be noted that this derivation assumes no specific law of settling beyond the three postulates; therefore this method of analysis may be used under any settling conditions for which the relation between particle diameter and settling time can be experimentally determined, whether or not Stokes' law is applicable.

Measuring Amount of Material Settling Out. The next question to be answered is: How can the amount of material reaching the bottom of the sedimentation column in a given time be measured? There are several ways of doing this, but one of the simplest is to measure the hydrostatic pressure just above the bottom of the column. This is the method used by Wiegner in his instrument for silt analysis (*4*). Since the particles are neither accelerating nor decelerating, their entire weight must be supported by the liquid and they can be considered as if they were stationary and suspended in the liquid. Obviously, in the latter case the pressure on unit area at the base would be equal to the weight of the column above it, which would be composed of the weight of the liquid plus that of the suspended particles. When the particles settle down past the point of pressure measurement, the pressure decreases. The decrease is only equal to the apparent weight of the particles suspended in the liquid because a volume of liquid equal to the volume of the settled-out material flows into the column. Thus it can be stated that the change in pressure at the point on the wall of the sedimentation column is directly proportional to the amount of material that has settled past this point.

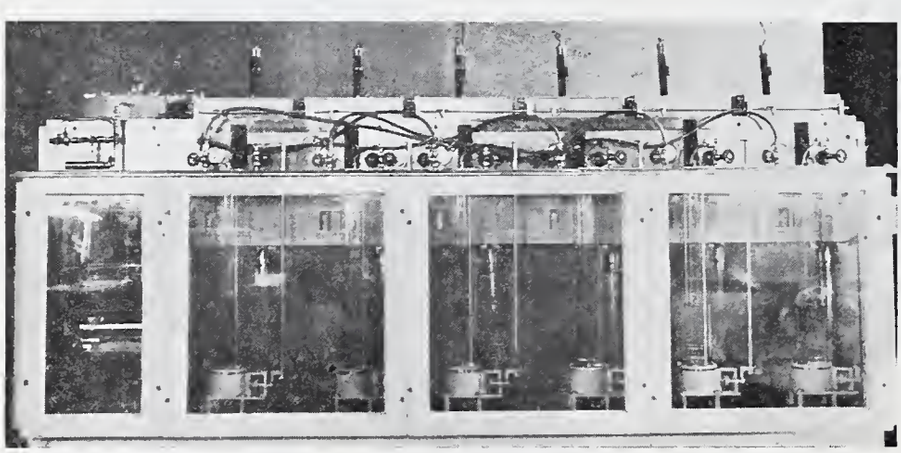


Figure 5. Photograph of Apparatus before Installation

Since sedimentation instruments operate on the assumption that the suspended particles obey Stokes' law, a study of Equation 1 and the range of its validity brings out the following as conditions which must be fulfilled if accurate results are to be obtained:

1. The viscosity of the fluid must remain constant.
2. The densities of both the fluid and the material under test must not vary.
3. The relative velocity between the fluid and the fastest moving particles must not be over a certain critical maximum—i. e., the velocity above which local turbulence is set up.
4. There must be no thermal convection currents to upset equilibrium.

Conditions 1, 2, and 4 all point to one conclusion—namely, that temperature must be very carefully controlled.

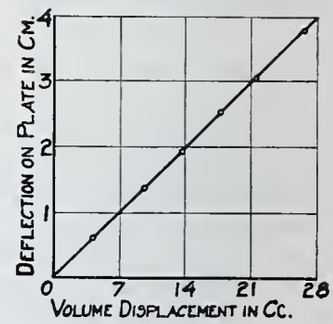


Figure 6. Calibration Curve for Pressure Unit

Description of Apparatus

The apparatus (*1*) finally constructed depends upon the principles just discussed. It consists of six sedimentation units, each equipped to measure and record the change in pressure at the bottom of the column. These units are in one housing, using a common source of time axis movement, a common liquid supply and removal system, and a common system of temperature control. A schematic diagram of the arrangement is seen in Figure 4.

Each unit consists of a glass-walled sedimentation tube S, which contains a stirring rod SR. The tube is closed at the bottom by a brass casting, containing a small pressure-measuring orifice. This is connected to the pressure cell P by means of the tube T. The connection can be opened or closed by means of the valve V, whose operating handle projects out through the top of the case. The pressure cell P is composed of a rigid outer case containing a metal bellows B. The change of pressure acting on the closed bottom of the bellows causes it to move. The pressure due to the normal column of liquid is counterbalanced by the mass CB which is fastened to the bottom of the bellows. The movement of the bellows is indicated by the tilting of the mirror M_1, to which are fastened three needle-point supports. One, N_1, bears on a glass surface on the top of a pedestal fastened to CB and therefore to the bottom of the bellows. The other two, N_2, rest on a bracket which is fastened rigidly to the case of P, and therefore has no movement. The tilting of the mirror is recorded by a beam of light, whose source is a small globe E. This is focused on the slit SL by means of the lens L_1. The beam passes through the lens L_2, to the mirror M_1, then back through L_2 which brings it to a sharp focus on the lantern slide plate LS, housed in a light-tight plate box PB. The plate rests in a carriage which is given a motion perpendicular to the plane of the paper through the medium of the clock shaft C and a train of gears. The operating range of the beam of light is shown by the dotted lines LR_1. For lower pressures the ray travels forward toward the settling tube S. As it leaves the front edge of the photographic plate it passes onto the mirror M_2, which reflects it onto a small strip of ground glass G visible from the front of the apparatus. The position of the ray in this state is shown by the dotted line R_2. The intensity of the light

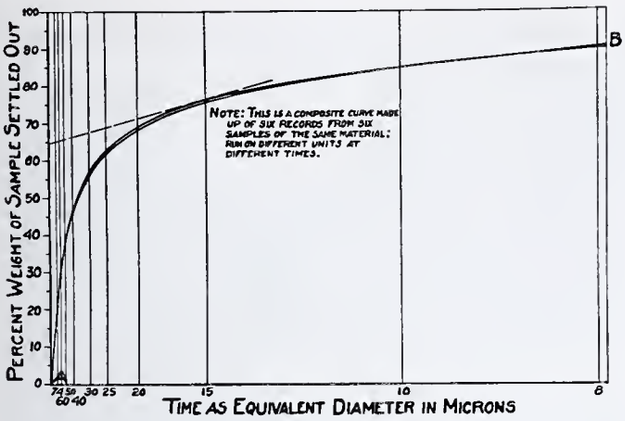


Figure 7. Analyzing Screen

is controlled by a small rheostat and milliammeter located near the ground-glass window *G*. A stationary mirror is also provided which projects a fixed light spot on the plate. This spot traces a reference line which defines both the zero value and the direction of the abscissa independent of the rough edge of the photographic plate.

Six of these units are housed in one case which has a set of windows *W* running along the entire front, so that the settling chambers can be inspected at all times. The case is divided into two parts by a partition wall *PW*, which comes down low enough to protect the optical system from too much stray light. At the upper part of the sedimentation compartment there is an air inlet *ID* running the entire length of the case, with numerous ports to supply air. The corresponding outlet duct *OD* is in the lower right-hand corner of the case. These ducts are connected with a blower and a heater box outside the case. The electric heater units are controlled by a sensitive thermoelement located inside close to the sedimentation tubes. Thus the entire case is operated as an air-bath thermostat. Figure 5 is a photograph of the apparatus as it appeared before installation.

The clock shaft *C* runs along the entire length of the case and drives the carriages of all the units. The power is supplied by a small synchronous motor which furnishes a reliable as well as a convenient means of obtaining the movement of the time axis.

Liquid System. In the operation of the apparatus it is necessary to have a supply of the liquid at the correct temperature and also a removal system to take care of the liquid in the sedimentation chambers after analyses are completed. To meet this first requirement a thermostated storage tank is provided. The tank is arranged so that air pressure can be supplied to it and a system of piping carries the liquid to each sedimentation chamber. Thus by opening a valve the desired unit can be filled with fresh liquid. The used liquid is removed by applying suction to the hollow stirring rod. It is then stored in settling tanks for several days, after which the nearly clear liquid passes though a filtering system and is returned to the thermostated tank for further use. Care is taken to remove any traces of moisture introduced by the sample. A careful watch is maintained to see that no trace of flocculation appears in any of the units, and a suitable deflocculator is added as necessary to maintain the concentration well above the limit of safety.

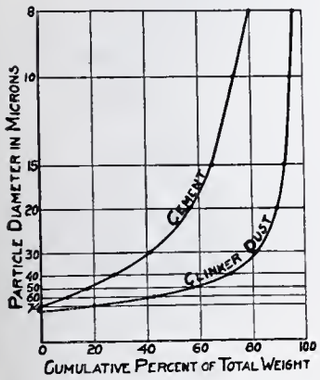


Figure 8. Method of Plotting Size Distribution Data

Particle diameter *vs.* cumulative per cent of total weight

Accessories. The necessary instruments for standardizing the liquid and for determining the density of the samples are located inside the case because of the desirability of making these determinations at the working temperature. They are so arranged that the measurements can be made from the outside. The viscosity is measured with a capillary tube pipet. The densities of the liquid and of the samples are determined with the help of an analytical balance mounted on the left end of the case. A fine wire is carried down from one pan into the inside of the apparatus. Liquid densities are obtained by means of an Invar plummet suspended from the wire and immersed in a beaker of the liquid. Sample densities are obtained by hanging a small bucket from the wire. A small amount of the material is placed in the bucket and weighed. The bucket is then immersed in the beaker of the fluid, the density of which has just been determined, and weighed again. Obviously, the sample density can be calculated from these two weights. A very necessary precaution in this procedure is to insure that no air is trapped in the sample when it is weighed in the liquid.

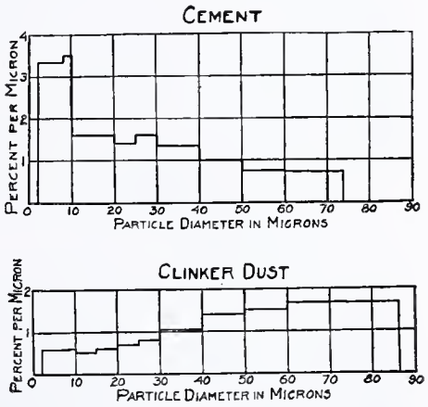


Figure 9. Method of Plotting Size Distribution Data

Method most employed in representing Microneter data

In order to facilitate operation, the apparatus is located in a dark room. This makes the changing of the plates a very simple matter, and facilitates temperature control because the entire room is used as a secondary thermostat and its temperature is held constant within ±0.5° F. (±0.3° C.)

Calibration and Operation

Several factors govern the choice of the liquid to be used in the sedimentation. Most of these depend upon the sample itself; therefore a suitable liquid must be selected for each class of material. The sample and the liquid must have no chemical reaction, the liquid must not induce flocculation of the sample, and the rate of fall of the larger particles of the sample must be lower than the value at which Stokes' law ceases to apply. Arnold (*2*) found that the maximum allowable radius is

$$r_{\max.} = \frac{0.6\eta}{v\sigma_m} \tag{7}$$

Combining this with

$$V = \frac{2g(\sigma - \sigma_m)r^2}{9\eta} \tag{1}$$

and solving for viscosity

$$\eta_{\min.} = \sqrt{0.37 r_{\max.}{}^3 g\sigma_m(\sigma - \sigma_m)} \tag{8}$$

This is the minimum allowable viscosity for the liquid to be used with a sample whose largest particles have a radius $r_{\max.}$ Care must be taken to stay well over this limit.

It is necessary to know how much the beam of light deflects because of a given pressure change in the sedimentation chamber. This is easily and accurately determined by suspending a series of metal rods of known volume in the sedimentation liquid, and measuring the deflection produced by each in turn. The displacement of a given volume of liquid increases the head, or pressure, at the measuring orifice a definite amount. The calibration obtained in this manner is an over-all one, and thus includes all errors in the pressure element, optical system, etc. Figure 6 is an actual calibration curve for a unit. The deviations are so small that a

straight-line calibration may be assumed. With this value determined it requires simply routine calculation to secure the sample weight for each unit so that the pressure ordinate on the plate will have the desired scale. Likewise the position of the initial liquid level is calculated so that when the sample is added the recording spot will fall on the plate. When this initial level is known the corresponding position of the point of light, which under these conditions appears on the ground-glass window G (Figure 4) is marked and this mark is later used to indicate the correct level when the sedimentation chamber is filled with fresh liquid. This is a very accurate method of setting the initial level, for the spot of light is sensitive to about 3 drops of liquid.

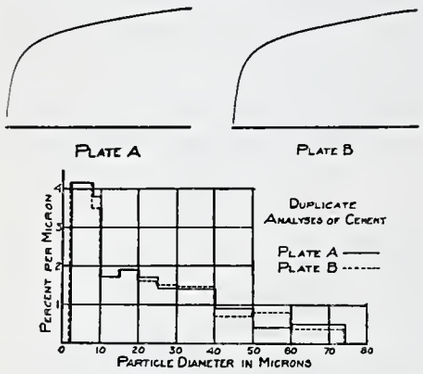


Figure 10. Duplicate Analyses of Cement

Operation of Apparatus. The sedimentation chamber is cleaned from the last run, refilled with liquid to the correct level, and allowed to establish equilibrium.

The liquid level height is readjusted by means of a medicine dropper until the spot of light is at the correct position on the front ground glass. The light is then turned off.

The room is darkened and the plate carriage is loaded with the correctly labeled plate. The plate box cover is replaced and the rest of the operation is carried on with normal illumination in the room.

The valve between the sedimentation chamber and the pressure unit is closed and the sample is emptied into the chamber.

The sample is stirred vigorously.

The plate carriage gear train is then thrown into mesh and the light in the optical bench turned on.

A few more strokes are made with the stirring rod and the valve is opened immediately after the completion of the last stroke. The stirring rod remains in position throughout the run.

Nothing is disturbed for 3.25 hours. At the end of this time the recording light is turned off, the valve is closed, the photographic plate is removed, and the unit is ready to be cleaned for the next run.

The position of the movable spot on the ground-glass window before the sample is added is determined so that the addition of the calculated weight of sample causes this spot to coincide in position with the stationary reference spot at the instant the run commences. The reference line, therefore, locates the origin of the curve, and is used for that purpose during the analyzing process.

Analysis of Plates. After development, the plates are analyzed by the tangent method previously discussed. To increase the speed of this work a projector is employed which projects the image of the curve, magnified about 4 diameters, upon the under side of the opal-glass screen. The plate may be moved in directions parallel to the two axes by means of the adjusting rods seen projecting up through the top. The screen is ruled as shown in Figure 7. The y axis is graduated to show per cent settled out, since this is directly proportional to change in pressure. The x axis is of course the time axis, but is graduated as diameter in microns, using the relation of Equation 3, $r = K/\sqrt{T}$.

The technic of analysis is as follows: A plate is placed in the projector, its image appearing on the screen as in A-B (Figure 7). The position of the plate is then adjusted until the zero reference line is parallel to the abscissa and the upper edge of this reference line passes through the origin on the screen. The y intercepts of the tangents to the top edge of the curve at the points of intersection of the micron lines are then obtained and recorded on the analysis sheet. These values with their corresponding diameters give directly the familiar cumulative weight or size table.

Since all the constants of the Stokes' law equation are determined in the routine operation of the apparatus, the theoretical value of K may be readily calculated. However, Stokes' law assumes spherical bodies, and the grains in a powdered substance deviate considerably from this assumption. Therefore, it is desirable to make an experimental determination of K. Briefly, this was done by carefully settling out a very small fraction of material, all the particles of which had a uniform settling rate, and measuring the average diameter of these particles by the microscopic method (*5*). This was repeated for three other sizes of particles. The separation was made by repeated sedimentations in one of the tubes of the apparatus with standard conditions of viscosity and density. The results are shown in Table I.

Table I. Experimental Determination of K

Sample	Settling Time of Particles Minimum		Maximum		Statistical Diameter	Predicted Diameter, Stokes' Law	Shape Factor
	Min.	*Sec.*	*Min.*	*Sec.*	*Microns*		
A	5	15	5	30	56.6	44.2	1.28
B	18	0	18	45	29.0	23.9	1.22
C	70	0	72	0	16.2	12.2	1.32
D	315	0	330	0	7.3	5.7	1.28

It is interesting to note the agreement between A and D, the largest and the smallest fractions, and also that the average of the four is 1.275. An additional factor was considered before finally determining K. The results from the apparatus were to be correlated with the regular standard sieve analysis of the larger particles in order to obtain the complete size distribution of the sample. Screen sizes are given as the dimension of the square opening between the wires. Therefore, the microscopic determination was also made of the average size of particle just passing a standard sieve. It was found that the ratio of the microscopic diameter to the screen opening gave an average value of 1.22. Since sieve sizes are so well established, it was decided to reduce the results from the sedimentation analysis to the sieve size basis. Thus Equation 3 has the following forms:

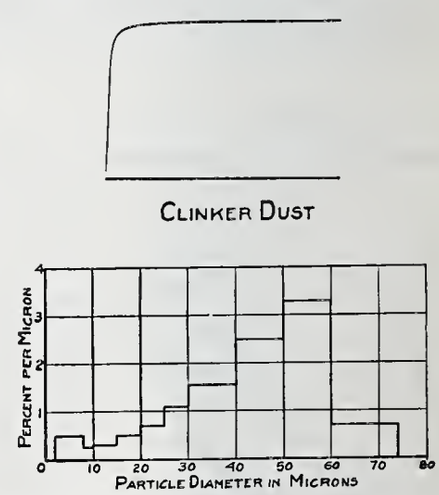


Figure 11. Analysis of Clinker Dust

(*a*) Calculated from the physical constants $D = \frac{105}{\sqrt{T}}$

(*b*) Determined by experiment $D = \frac{134}{\sqrt{T}}$

(*c*) The latter reduced to sieve size basis $D = \frac{110}{\sqrt{T}}$

(*c*) is the form of the equation used in final analysis. Note the small difference between (*a*) and (*c*).

Sample Analyses. There are many graphical methods of plotting size distribution data. Figures 8 and 9 show two alternative schemes. Figure 8 is the familiar cumulation per cent *vs.* diameter curve, which is convenient for many

purposes but is not very suitable for studying the amount of material of given size present. Figure 9 illustrates a more useful diagram, and is the one most employed in representing the Microneter data. In constructing this form of curve one precaution must be taken: the size increment must be kept the same over the entire range of diameters. If this is not done the curve shape is very misleading. It will be noted from Figure 9 that apparently the minimum diameter is 2 microns. This is a statistical minimum—i. e., a study of some special 30-hour plates showed that there was no significant fraction of this particular material that had a diameter less than 2 microns. Figure 10 shows duplicate analyses of portions of the same cement, and demonstrates the consistency of the results obtained with the Microneter.

Figures 11 to 13 illustrate the great variation in size distribution found in fine powders. Each represents the analysis of a different sample of material. However, all the samples passed 100 per cent through the 200-mesh sieve and thus with normal technic there would have been no further way to determine their relative fineness. Each figure consists of the reproduction of the original plate and the per cent per micron curve calculated from it. If the total surface is taken as a measure of the average fineness, the sample of Figure 13 is about four times as fine as that of Figure 11. These curves illustrate the importance of obtaining data on the size distribution of such materials, because this large difference in surface implies great differences in energy required for grinding, in speed in subsequent physical or chemical reaction, and in many properties of interest to the producer or user of such products.

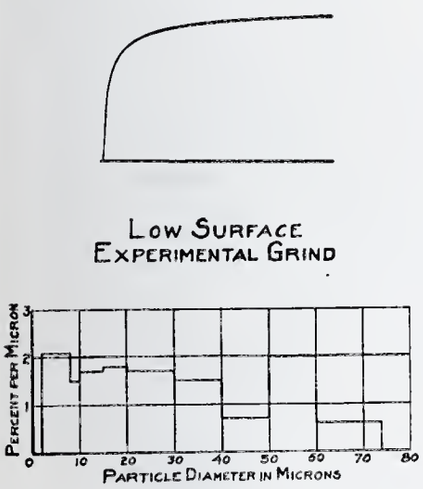


Figure 12. Low Surface Experimental Grind

Conclusions

The apparatus described has been in operation for several years, during which time it has been used to analyze more than five thousand samples. The capacity, 36 samples a 24-hour day, is great enough for work where more than the occasional sample has to be analyzed. Where the maximum capacity is not necessary, it has been found that one skilled operator can complete 18 analyses per 8-hour day, including preparing the sample, operating the machine, developing the plates, analyzing them, and calculating the results. The accuracy of these determinations of subsieve sizes is at least comparable to, if not considerably better than, that obtained with standard sieves of 200-mesh and coarser which are universally employed to analyze materials of larger particle diameters.

The apparatus has demonstrated its adaptability for use with a wide range of substances. Although designed primarily to analyze cement samples, it has been successfully employed for materials ranging in specific gravity from 2.7 to 3.7, including cement clinker, cement rock, diorite, limestone, silica, sand, and slag.

Experience has demonstrated that the optimum size range for one plate is about 10—i. e., the largest particles in the sample are about 10 times the diameter of the smallest size for which a reading is desired (but not necessarily the smallest particles present). There is no reason, however, why the position of this range cannot be varied over wide limits by proper control of the viscosity of the liquid and the density difference. The practical upper limit of size is controlled by the possibility of securing a uniform mixture, which becomes increasingly difficult as the viscosity is raised. The lower limit is governed by the allowable length of time for a run, and by the entrance of colloidal effects, such as Brownian movements.

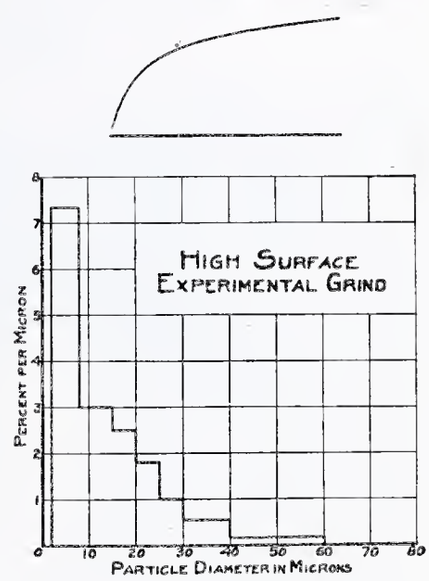


Figure 13. High Surface Experimental Grind

The Microneter has satisfactorily met the five specifications originally set up as the prerequisite qualities needed for a successful instrument.

Acknowledgment

The writer wishes to acknowledge the whole-hearted support given by John Treanor, president of the Riverside Cement Company, and by Hubert Woods, director of the Research Department of the same company, for which this work was undertaken.

Albert E. Myers assisted greatly during the early stages of development. Emory L. Ellis operated the instrument for many months, completing several thousand analyses, and put it on a producing basis. Howard Starke, who has had complete charge of the instrument for the past three years, has contributed many improvements in construction and operating technic which have decreased the labor required while increasing the speed and reliability.

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Japan's Chemical Industry Forges Ahead. That the organized effort of Japan to make itself self-sufficient in chemical products for which it formerly depended on outside sources is meeting with success is indicated in a report to the Commerce Department. As a result of the increase in plant capacities and the devaluation of the yen, Japan is now able to compete with other chemical manufacturing countries in world markets, particularly in the Far East.

Unitized Gas-Analysis Apparatus[1]

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Constant-pressure gas-analysis equipment has been devised which utilizes the advantages and discards the disadvantages of the Hempel and Orsat systems, combining the flexibility and adaptability of the one with the convenience, compactness, and rapidity of the other. The apparatus consists of complete self-contained units that fasten together to form any desired assemblies of the Orsat type.

A number of improvements have been devised that have simplified gas-analysis equipment and its manipulation, and increased its accuracy, convenience, and usefulness.

Heretofore, constant-pressure gas-analysis apparatus has been of two general types, best designated by the names of Hempel and Orsat.

The Hempel type is characterized by the use of a number of individual absorption pipets, each in its own support or frame, which are connected and disconnected in turn to the gas buret. Besides being accurate, this system is flexible and adaptable. Different kinds of gas mixtures can be analyzed without change of equipment. New or special absorbents can be employed in additional pipets without any limitation as to number. New and better devices can be added to the equipment without discarding the old. The apparatus, however, is bulky and not readily made portable, in spite of changes in the direction of more compact pipets, such as described by Augustin (*1*). Moreover, it is inconvenient and time-consuming because of the many connections and disconnections.

The familiar Orsat type is characterized by having a fixed frame, a fixed number of pipets, and a fixed manifold. This combination overcomes the disadvantages of the Hempel type, but only at the sacrifice of almost all flexibility and adaptability and frequently of considerable accuracy.

The unitized gas-analysis equipment described in this paper combines the advantages of both the Hempel and Orsat types and eliminates their disadvantages. It is the result of an effort to eliminate the objectionable features of traditional gas-analysis apparatus and to develop a more satisfactory analytical tool. No less than a fundamental redesigning of apparatus has been found necessary to meet the needs of modern gas analytical work. The changes introduced have increased simplicity, accuracy, convenience, or usefulness.

Recent Literature

Aside from descriptions of minor changes or improvements, the recent literature contains but few articles that deal with the fundamental design of gas-analysis equipment, perhaps the best known of these, especially in America, being Shepherd's (*13*).

The apparatus described by Shepherd is an improvement over the usual Orsat apparatus in such details as a metal framework that permits greater accessibility to the various parts, a buret illuminator, a more efficient bubbling pipet for the removal of oxygen, and a special stopcock for controlling the flow of mercury. It is, however, subject to a number of criticisms that have undoubtedly militated against its adoption. It is somewhat complicated in construction and operation. Its range is limited by the absence of a copper oxide tube. The large number of stopcocks—two for every pipet—necessitates much extra handling, increases the cost of the apparatus, and multiplies the danger of leakage. Furthermore, it increases the amount of dead capillary space, which must be corrected for by time-consuming "simple arithmetic" or additional operations. The manifold is built up of T-bore stopcocks after the manner suggested by Pfeifer (*12*), who devised this arrangement for the purpose of making the manifold flushable. It is not, however, flushable in the modern sense, as are manifolds built up of 120° three-way stopcocks (*2*, *11*) or of three-way stopcocks having special L- or V-bores (*5*, *7*). The short length of the buret, if not accompanied by any loss of accuracy, has made it more confusing to read, as it is graduated in fifths of a milliliter instead of in tenths. The water jacket is unnecessarily expensive because of its large diameter and the additional glass-blowing involved. The apparatus is heavy and not readily made portable, being designed for laboratory work only.

Another apparatus developed in this country is that designed for use in the laboratories of the subsidiary companies of the U. S. Steel Corporation (*5*). To eliminate the need for more than one apparatus for different kinds of gas mixtures, all the devices in general use on different Orsat apparatus are combined into one assembly. This assembly has six absorption pipets, a slow-combustion pipet, an explosion pipet, and a copper oxide tube, together with the necessary electrical equipment. This arrangement necessitates the purchase of much equipment that is but seldom if ever used, and aside from the introduction of a new flushable manifold (*7*), presents no improvement of fundamental design.

A greater divergence from the traditional Orsat apparatus is that developed abroad by Bahr (*2*). The apparatus is made in two parts, one for the absorption operations and one for the combustion analysis. Each is provided with its own buret, so that a second sample can be undergoing absorption while the first is undergoing combustion. Combustion is effected with two copper oxide tubes, one being heated to 300° C. for oxidation of hydrogen and carbon monoxide and the other to 900° C. for oxidation of methane and ethane. The accessory apparatus for flushing and heating the two copper oxide tubes makes this apparatus too bulky and the operations too involved.

A more compact arrangement described by Vossieck and Schmitz (*15*) contains two burets but only one copper oxide tube, which is used for hydrogen and carbon monoxide. Methane, mixed with air or oxygen, is oxidized over a hot platinum wire in a quartz capillary. In the absence of ethane, the reduced copper oxide may be simultaneously reoxidized. Another apparatus containing two burets is described by Burkhardt, Fischer, and Frank (*3*). One buret is of smaller volume than the other and is used for the combustion work.

An interesting article by Neumann and Strähuber (*10*), which deals with the design of gas-analysis apparatus of the Orsat type, presents complete details of the apparatus used by the Warmestelle at Düsseldorf, including scale drawings of the different parts. It also gives an unusually thorough consideration of capillary error, but presents no important changes in fundamental design.

No successful effort apparently has been made heretofore

[1] Patents applied for.

to combine the flexibility and adaptability of the Hempel system with the compactness, convenience, and rapidity of the Orsat system. A start in the proper direction, however, has been made by discarding the fragile, inflexible, one-piece manifold. For example, Bahr (*2*), Vossieck and Schmitz (*15*), and Ott (*11*) have adopted pipets terminating at the top in three-way stopcocks of the 120° type and have shifted the rubber connections from the vertical branches to the main line of the manifold.

Advantages of Unitized Apparatus

Both precision and technical assemblies of the unitized gas-analysis equipment are shown in the illustrations. Precision assemblies are capable of the most exact work that can be performed with assemblies of the Orsat type. Technical assemblies are limited to a lower degree of accuracy by the shorter length of the buret and the absence of a compensator. A technical assembly is made portable by simply being provided with a carrying case.

The chief departure from the traditional Orsat design is the division into individual self-contained units, each including its share of the framework and manifold. This change permits the building of any assembly, from the simplest one-pipet type to the more complex several-pipet types, from standard units. The same reaction units are used in both precision (laboratory) and technical (portable) assemblies, and an assembly can be expanded at any time by the addition of more units. For example, a fractional-combustion or copper oxide unit can be added without expensive alterations in manifold or framework. Devices embodying future improvements in apparatus or technic can be added when developed without discarding an expensive piece of equipment.

Referring to the apparatus designed for the U. S. Steel Corporation (*5*), it is evident that a corresponding assembly can be built from the new units. Certain advantages are immediately apparent. The unitized assembly is not limited by the framework or manifold and can therefore be expanded or contracted at will to meet special requirements. The operator can arrange the units in whatever order he considers best—for example, the buret can be placed at either the right or the left end of the assembly, or two burets can be incorporated. These can be of different designs to deal more adequately with different kinds of gas mixtures or to conduct the combustion operations more accurately; or, they can be used to permit taking in a new sample and subjecting it to the absorption procedure while the old is undergoing the combustion analysis. Other incidental advantages, such as an all-metal framework, greater accessibility of parts, greater ease of removal and cleaning of glassware, elimination of the unnecessarily large size of the instrument panel and safety-glass shield, greater flexibility, smaller fragility of glass parts, elimination of dead capillary space, etc., will be apparent from the description of the equipment.

Framework

The framework is entirely of metal, employing aluminum alloys wherever possible. Sturdiness, durability, and full accessibility to all parts have been achieved. All parts are symmetrically designed to permit standardization and interchangeability.

The framework allotted to each reaction unit consists of two parts. One is a back piece, bolted to identical pieces in other units or to a clamp on a frame support, from which extends a vertical rod carrying a phosphor-bronze clip for securing the top of the reaction vessel. The other is a vertically adjustable shelf piece, cup-shaped and lined with felt for protection of the absorption pipets.

The two vertical frame supports for technical assemblies consist simply of half-inch (12.7-mm.) aluminum rods about 50 cm. long, imbedded in cast-aluminum feet. They can be screwed or bolted to any appropriate base, such as the bottom of a carrying case, and are provided at the top with removable bottle-rests which also serve as guides when slipping a case down over the assembly.

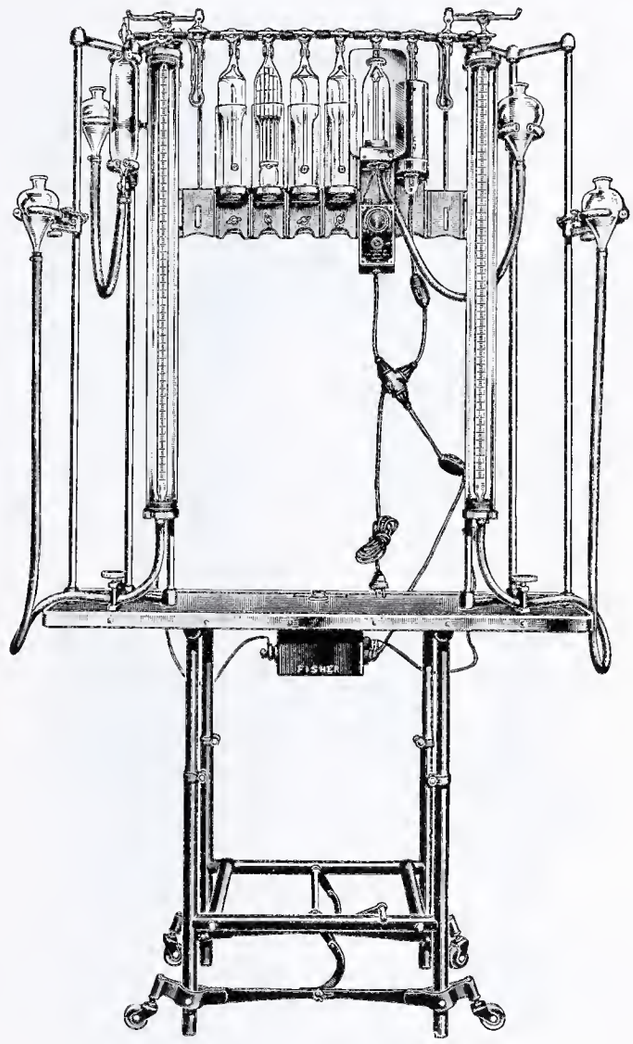

Figure 1. Unitized Precision Time-Saver Gas Analyzer

Each support for precision assemblies consists of three parallel stainless-steel rods, about a meter long, in a staggered or V-formation with two rods in the line of the reaction train and the third or middle rod set back about 75 mm. They are held together by a light removable aluminum top piece, and by brass feet which are bolted or screwed to a table or other appropriate base. The three rods at each end of the assembly support the train of reaction units, the measuring unit, the sampling bulb, and the various leveling bulbs.

Manifold

The manifold is built up of stopcocks which are integral with the various pipets or other reaction vessels, joined together by horizontal rubber connections. This permits a maximum of flexibility and adaptability with a minimum of fragility.

The number of rubber connections has been decreased. For example, in the well-known Bureau of Mines assembly (*4, 6*) there are ten rubber connections, one of which has been eliminated in later models; in the corresponding unitized assembly the number has been reduced to seven. In general, the number of rubber connections with which the sample can come into contact during the analysis proper has been reduced

by one in all models not having a copper oxide tube, and by two in all that do include such a device.

Dead capillary space in the vertical branches is practically nonexistent. The reagents can be drawn up almost to the stopcock. Unlike the U. S. Steel Corporation apparatus referred to above, this can be done without the absorbents

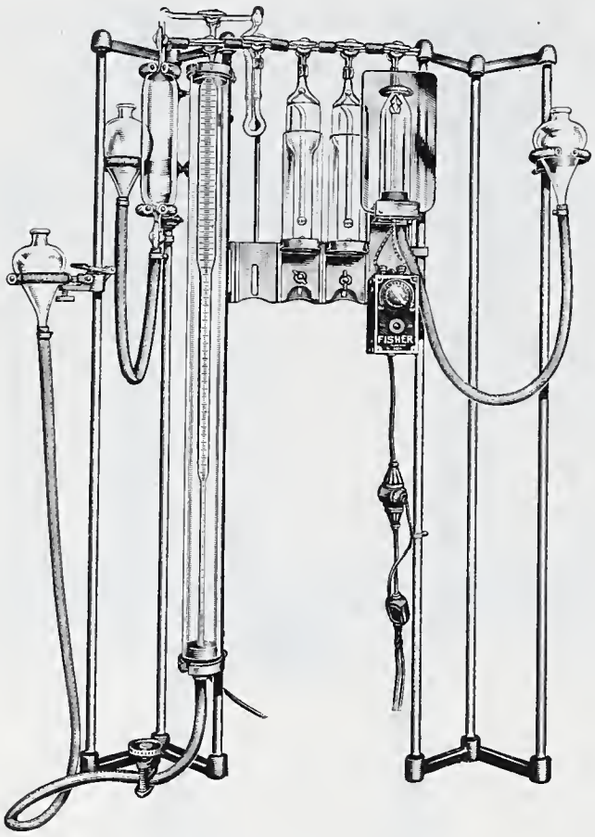

Figure 2. Unitized Precision Mine-Air Analyzer

coming into contact with rubber connections. Also, the rubber connections are not continuously subjected to the action of absorbents or their vapors when the apparatus is idle.

For elimination of capillary error the manifold should be filled with nitrogen at the beginning of an analysis. A more awkward and time-consuming procedure is to fill the horizontal capillary with acidulated water or mercury from the slow combustion pipet or from an auxiliary pipet. Since such devices as manometers and copper oxide tubes can be flushed only with inert gas, the use of liquids to eliminate capillary error is not to be recommended. On the other hand, it is desirable to be able to use acidulated water for washing out any absorbent drawn into or beyond the bore of a stopcock, without dismantling the assembly and without loss of the sample.

The new manifold is more perfectly flushable and more easily cleaned than any other known to the author. This has been achieved by its straight-line design and the use of straight-bore three-way stopcocks.

The principle of operation of the straight-bore three-way stopcock is the same as that of the 120° stopcock, but the construction is different. Two of the arms are in the same straight line, with the third at right angles. The plug has a single, straight, eccentric bore. This construction makes it possible to pass a length of cotton-covered wire completely through the manifold from one end to the other without removing any plugs. Other flushable manifolds have three-way stopcocks with bores of an L- or V-shape (*5*, *7*).

All stopcocks used in the unitized manifold are identical in construction and operation. The four-way stopcock on the fractional combustion unit is but an adaptation of the straight-bore three-way stopcock, and is manipulated exactly like the others. Every stopcock has the same relative position, with two arms horizontal, the third downward, and the handle to the front. This simplification aids the operator to manipulate the stopcocks without examining them to determine the position of the plug. The usual precision Orsat apparatus has three or more different kinds of stopcocks—the Shepherd apparatus has five, not including the control stopcock at the lower end of the buret—and these are sometimes placed with handles to the side instead of to the front.

Burets

All burets are provided with one stopcock at the top. Their symmetrical construction permits an unusual flexibility of adaptation.

Precision Burets. Reducing the number of stopcocks on the precision buret to one permits it to be raised relative to the reaction train, and to be read with greater ease and comfort. It also permits increasing the length of the graduated section, thus making the spacing of the graduation marks somewhat greater and contributing to the accuracy and ease of reading.

The change has also decreased the fragility of the buret, and lowered maintenance cost. Fewer rubber connections result in a gain in flexibility and in freedom from strains.

Precision burets have an over-all length of 87 cm., a graduated section of about 70 cm., and a capacity of 100 ml. The graduations are black, more permanent than the usual white ones, and standing out in sharper contrast against the background afforded by the water jacket. The graduations include the bore of the stopcock.

The latest style of graduations is used. Whole milliliter marks extend completely around the buret, for elimination of parallax, and even milliliter marks are numbered. The other marks extend around a portion of the buret but not halfway. This style of graduations is as accurate as the so-called "U. S. Bureau of Standards style of engraving" and is more rapid and easier to read, because immersion of the buret in water causes magnification or even the appearance of additional images or reflections of each graduation mark. If half-circles are present the resulting maze of marks and their images is distracting and tiresome to the eye, particularly as the marks are usually placed much closer together than recommended by the Bureau of Standards (*14*). However excellent half-circles may be on other pieces of laboratory glassware, they constitute a decided handicap on gas burets.

Precision burets are of two principal models. The universal model is of uniform bore, graduated in 0.1 ml., and is suited for the analysis of any kind of gas mixture. The other model is designed for use with mine air and similar gases that have small percentages of some components. It is made in three sections of different diameters, conforming in this respect to the specifications of the U. S. Steel Corporation (*5*). The top section has a capacity of 72 ml., graduated in 0.2 ml.; the middle section, 22 ml. in 0.1 ml.; and the bottom section, 6 ml. in 0.05 ml. A third model, with a narrow 50-ml. upper part and a 50-ml. bulb at the bottom, is sometimes advantageous in conducting combustions.

Technical Burets. Technical or portable burets are about 45 cm. long, of 100 ml. capacity, and of three different designs. The universal model is of uniform-bore Schellbach tubing, graduated in 0.2 ml. The flue-gas model has a 50-ml. bulb at the top and a lower portion of Schellbach tubing graduated in 0.1 ml. The purity model is of clear glass with a 94-ml. bulb in the middle, the top and bottom 3-ml. sections being graduated in 0.05 ml. It is designed for determining

the impurities in cylinder gases, either directly or by difference.

Placing the intake stopcock of earlier portable Orsat apparatus at the top of the technical buret increases the accuracy of the assembly, as the sample can be drawn directly into the buret instead of first traversing the manifold. Hence, all the sample is successively treated in the absorption pipets, as none is trapped in the manifold beyond the particular pipet in use. The graduations include all of the capillary stem and the bore of the stopcock.

Leveling Bulb Support. The leveling bulb of a precision buret is supported by a movable split-ring support with an automatic locking device which replaces the thumbscrew on earlier supports. A slight pressure with the thumb releases the support, which can then be moved up or down. Releasing the pressure automatically locks it securely in place. It is provided with a simple screw device for fine adjustment of the mercury level in the buret. This gives excellent control when balancing the pressure and when drawing the reagents up to the mark. The leveling bulb support will doubtless find acceptance in many laboratory set-ups other than gas-analysis apparatus.

An oversize screw clamp, with large knurled handle, controls the flow of mercury during combustions and can also be used to draw reagents up at a slow controlled rate. It is screwed permanently in place on the base of the apparatus.

Frosted-Back Water Jacket. The back of the water jacket in precision assemblies is etched. It provides a frosted background against which the black buret marks stand out in sharp contrast. It also diffuses the light and eliminates distracting images and distortions.

The buret is located in a central position in front of the axis of the water jacket, where it can be viewed without sidewise distortions caused by different depths of water.

The combination of the frosted back of the water jacket, the front-central position of the buret, and the back-central position of the compensator tube causes the formation of longitudinal light-images which give the back of the buret an appearance resembling that of Schellbach tubing. When the illuminator described below is used three colored vertical lines are formed: a central ribbon of about the same size as that in Schellbach tubing, which quickly centers the eye, and two narrow side lines which break sharply with their reflections on the mercury meniscus. These sharp breaks can be used to determine the position of the top of the meniscus, as they are more readily perceived and are lower than it by a small constant distance corresponding to about 0.02 ml. An alternative method that may be preferred is to interpose a shield between the light and the water jacket with its lower edge slightly above the level of the mercury meniscus. This causes the meniscus to stand out in very sharp contrast against the background. Both methods are easy, accurate, and rapid.

Compensator

A compensator of the Pettersson type is employed with precision burets. It is simple, accurate, and easily used.

Compensator Tube. The compensator tube is held firmly in place directly behind the buret by a glass rod that projects from its lower end into an opening in the rubber stopper of the water jacket. It terminates at the top in a straight-bore three-way stopcock, which may be replaced with a T-bore stopcock, since it never requires flushing with a liquid. Unlike the stopcocks of the unitized straight-line manifold, it is placed behind and above that of the buret. Its lateral arms are longer than those of the other stopcocks, extending to the center of the adjoining "unit space." One arm is connected to the manometer and the other is left free for communication with the atmosphere.

Manometer. The manometer is of a new symmetrical design that permits placing it always between the buret and the train of reaction units, irrespective of the position of the buret. It is supported by a clip in the same manner as the tops of the reaction vessels. Its rubber connections are fully accessible, as none is encased within the water jacket.

It is more compact and has less dead space than its predecessors. The mercury level is not more than 2 or 3 cm. below the stopcock, which is itself a part of the manifold. In other words, it automatically approximates the elimination of capillary error that can be achieved with others only by the time-consuming technic (*13*, *16*) of drawing the gas out of the manometer and subjecting it to the same operations as the sample itself.

The arms of the manometer are of 1.5- to 2-mm. bore. The effect of impurities on the surface tension of the mercury (*13*) can be minimized by keeping the menisci covered with a film of water acidulated with sulfuric acid. The arms are placed close together to permit adjusting both menisci to the same horizontal level. A small, vertically adjustable metal clip, to the lower edge of which both menisci are brought, is helpful. The usual technic of bringing only one meniscus to a mark is objectionable because it does not compensate for variations in the volume of the manometer liquid, such as those due to temperature changes.

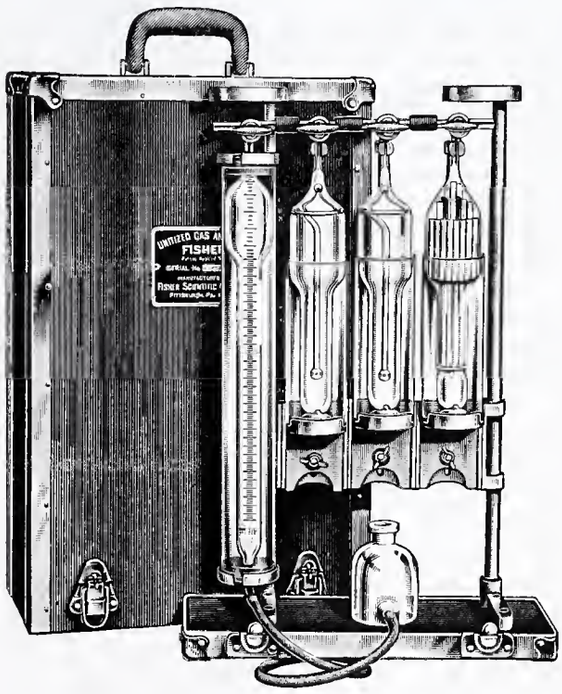

Figure 3. Unitized Technical Flue-Gas Analyzer

The manometer is provided with a simple check valve consisting of a spherically-true glass ball, that prevents accidental forcing of mercury and sample into the compensator tube.

When using the manometer, its stopcock should be turned once, after the buret has been roughly compensated to within 1 or 2 mm., so that the manifold can attain the same pressure as the buret. Close balancing can then be made. Contrary to a generally accepted idea, repeated turning is unnecessary. For example, should the manifold pressure be 2 mm. too high, the error introduced amounts to only 0.0026 ml. for every milliliter of uncompensated space. A milliliter corresponds to 56.6 cm. of 1.5-mm. bore capillary, or to 31.8 cm. of 2-mm. bore, and is therefore the approximate volume of a several-unit manifold; hence the error introduced would not be detectable on the buret. It is obvious that such turning of the

stopcock is unnecessary if the buret pressure, when communication to the manometer is first made, balances that in the compensator tube to within a few millimeters.

FIGURE 4. VALVE BUBBLER ABSORPTION UNIT

Turning of the manometer stopcock when balancing can be eliminated by substituting a T-bore stopcock for the straight-bore three-way stopcock. The buret, manifold, and manometer can then be simultaneously connected (*13*), and if desired can be kept so connected throughout the analysis, as ordinary manipulations do not cause the mercury in the manometer to escape into the manifold. Should, however, the volume of mercury be inadvertently changed, it is automatically compensated for by the technic of adjusting both menisci to the same horizontal level. Use of a T-bore stopcock can thus be used to expedite operations at only a slight sacrifice of flushability.

Absorption Pipets

The absorption pipets are free from the fragility inherent in the familiar Orsat pipets. No easily broken U-tube connection is present. The absorption part is placed above and within the expansion part, as in the Williams (*17*) apparatus. Instead of being of one diameter, however, the absorption part has an upper enlarged portion and a lower narrow portion. This decreases the height of the pipet and the range through which the absorbent level must move.

The top of each pipet is essentially conical. This shape minimizes the tendency to trap small bubbles of gas and aids the operator to draw the absorbent up to the mark without spurting it into the manifold. No etched mark is required, as the absorbent can be drawn up to the lower edge of the clip that secures the pipet just below its stopcock. Drawing the reagent closer to the stopcock is usually not necessary nor desirable.

The expansion part of each pipet is a simple cylindrical vessel having an indentation in the bottom for centering the lower end of the absorption part. It can be removed for the purpose of changing the reagent without removing any rubber connections in the manifold.

With the exception of fuming sulfuric acid, absorbents can be protected from the atmosphere by a layer of paraffin or mineral oil. This technic has long been in use by analysts of respiratory air but is not well known to others. Every expansion part is provided with a tubulature near the top which permits attaching a rubber expansion bag or a liquid seal. If this is used the junction between the absorption and expansion parts is closed with a short length of Gooch rubber tubing.

VALVE BUBBLER ABSORPTION PIPET. The valve bubbler absorption pipet contains a nonfloating automatic glass valve. It has both the valve chamber and the bubbling or gas conducting tube completely enclosed within itself. The construction is thus sturdier and less fragile than that described by La Condamine (*9*) and Francis (*8*). It is also neater and more pleasing in appearance, because of the general symmetry of its design.

The valve consists of a solid spherically-true glass ball. The fragile construction of other valves, which are made hollow in order to float, is not present; in fact, the valve is the least fragile part of the entire pipet. Likewise, the fragile projections previously necessary to guide the valves into their seats have been eliminated, as the ball can seat itself in any position.

Previous pipets have had an essentially cupshaped valve seat. This design, combined with the inverted cone- or pear-shape of the effective portion of the valves, has offered considerable resistance to free movement and has tended to cause sticking or freezing.

The valve seat in the new pipet consists simply of the upper end of a short vertical tube. The valve makes contact with it in such a narrow and but slightly inclined zone that there is no tendency to stick or freeze, although sticking might occur under unusual conditions, as, for example, under long-continued evaporation and caking of an alkaline solution around the valve. In such case, the ball valve could be liberated with the aid of a wire inserted from below, a feat impossible with older pipets.

On passing gas into the pipet the ball valve remains on its seat, making a gas-tight seal. The gas perforce is conducted by the bubbling tube into the absorbent, through which it ascends in the form of bubbles, which collect in the upper part of the absorption chamber, below the valve. A plug of liquid usually remains in the short tube whose end forms the valve seat.

On the return passage of the gas, the first portion kicks over the ball valve, together with the plug of liquid beneath it, to the adjacent wall of the valve chamber. It adheres to the wall because of the surface tension exerted by the liquid. The valve is now open and the gas comes up through it. As soon as the ascending liquid surrounds the ball the surface tension effect is eliminated, the ball falls back into its seat, and the pipet is ready for the next pass.

The end of the bubbling tube ends in a small bulb having several pinholes that break the issuing gas up into small bubbles.

The initial length of the column of liquid through which the bubbles pass is about 150 mm. It is decreased to about 80 mm. by the passage of 100 ml. of gas. These figures are larger than those for standard pipets of the usual design, indicating a longer time of contact between gas bubbles and absorbent. The time of contact is also somewhat increased by the fact that the narrowness of the lower part of the absorption chamber causes the downward flow of the absorbent to retard the upward rise of the bubbles.

CONTACT ABSORPTION PIPET. The contact pipet is filled with thin-walled glass contact tubes of different lengths which are staggered or cascaded to conform with the conical top of the absorption compartment, minimizing the usual unfilled space at the top. The tubes are held in place by a perforated porcelain disk. It is impossible to force a bubble of gas down any of them into the expansion part.

A modification of the contact absorption pipet contains some twisted copper strips among the glass contact tubes. It is used with cuprous solutions for the absorption of carbon monoxide.

Fractional-Combustion Unit

The fractional-combustion or copper oxide unit is a self-contained unit in exactly the same sense as are the absorption units. It is standard equipment that can be incorporated in any unitized assembly, without a special manifold or expensive changes in the framework. It occupies a "unit space" of the size allotted to an absorption pipet and is located in the same relative position. This position decreases the over-all height of the assembly and makes it as easily accessible and observed as any other unit. No troublesome heating of the stopcock or adjacent glass parts occurs.

The copper oxide tube is built integral with a single in-and-out four-way stopcock that replaces the two stopcocks used in other apparatus. This simplification has a number of obvious advantages.

It reduces the amount of stopcock handling required during the analysis. A single turn of 120° of the stopcock handle changes it from the by-passing position, with the copper oxide tube completely shut off from the manifold, to the in-and-out position, with the gas entering the tube through one bore and emerging through the other.

It eliminates completely the dead space in the manifold between the two stopcocks previously used, as there is no dead space whatever in the new stopcock. It also reduces the number of possible sources of leakage by eliminating both a stopcock and a rubber connection.

The small closed loop of the new tube makes it sturdier, more compact, and less fragile than the extended open loop of its predecessors. Its free space is smaller, because of reduction of capillary space and the use of small glass balls instead of glass wool for keeping the copper oxide out of the capillaries.

The electric furnace for the fractional combustion tube is small and compact. A short thermometer with a graduated range from 250° to 325° C. is inserted alongside the copper oxide tube and is held in place with a small metal clip that also indicates the proper position for the top of the furnace. The thermometer is easily read, as it is located at the eye-level of the operator.

Slow-Combustion Unit

All electrical accessories for the slow-combustion unit are enclosed in a small aluminum box, built integral with the shelf piece, which replaces large electrical panels present in earlier apparatus. It contains a specially wound transformer for stepping down the usual lighting current, a toggle switch, and a rheostat, and fits snugly into a unit space. A shield of safety glass is clamped in front of the pipet.

Aside from the integral stopcock, the pipet itself differs from the traditional design only in having its upper part terminating in a cone instead of a half-sphere. The traditional design has been retained as being most simple and reasonably free from faults. A single glass support carries the insulated leads to the coil.

Instead of the usual desultory loop, the coil forms a clearly defined inverted V, whose middle point is supported by a small extension of the central glass support. The small glass support keeps the platinum coil always in position without the disadvantages inherent in ceramic supports, such as those of uneven heating, insufficient heating, and absorption of gas (*13*).

The shape of the coil permits it to be inserted well up into the apex of the conical top of the pipet. This decreases the danger of an explosion because of delayed ignition or too rapid passage of gas.

Accessories

Sampling Bulb. The sampling bulb or sample container is provided with a straight-bore three-way stopcock at each end. Like the best of its predecessors, these stopcocks permit flushing and filling of the capillary connections at both ends without losing any of the sample or contaminating it with air. In addition they can be connected to any apparatus by either vertical or horizontal connections. They are arranged so that the sampling bulb can be connected to either end of a unitized manifold. It can be inverted so that the stopcock handles will always be in front, as the leveling bulb can be connected to either end.

The sampling bulb, when used with a precision assembly, is held by a split-ring support placed on the back rod of one of the upright frame supports. It can then be connected directly to the end of the unitized straight-line manifold—i. e., directly to the stopcock on the buret. The sampling bulb can be left in position during an analysis, as the stopcock at its top permits communication to the atmosphere, if desired. A second sample can be withdrawn without the necessity of reconnecting the sampling bulb.

Neon Buret Illuminator. The buret illuminator for precision assemblies consists of a straight neon-filled tube of the same length as the water jacket. A suitable standard transformer is used for stepping up the ordinary lighting current. The illuminator affords a soft, restful, uniform orange-tinted illumination, and used in conjunction with the frosted-back water jacket, which properly diffuses the light, it forms an efficient accessory for any precision assembly. It is considered superior to the recently available incandescent bulbs with filaments about 30 inches (76 cm.) long in that its light is cold and does not waver because of vibrations of the filament.

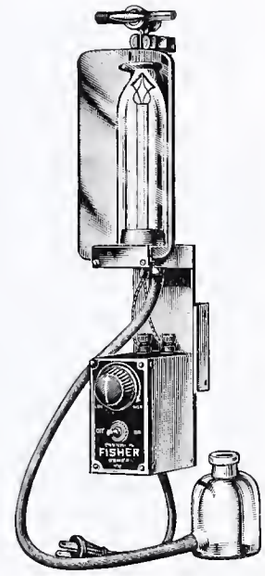

Figure 5. Slow-Combustion Unit

Carrying Case. The carrying case for portable assemblies is lowered over the assembly and clamps to the base to which the assembly is bolted. This design permits full accessibility to all parts of the apparatus when the case is removed. It is built of strong light plywood covered with black fiber, with edges bound in aluminum, and is provided with chromium-plated corners, catches, and hardware for the leather handle. The slip-proof, draw-bolt construction of the catches insures them against slipping and dropping the apparatus.

The carrying case is made in two sizes. The large size can hold an assembly of two burets and five reaction units or one buret and six reaction units. The smaller size can hold a buret and three pipets. Limitation to two sizes effects important economies in production.

Gas-Analysis Table. The adjustable and movable table shown in Figure 1 presents certain advantages for gas analytical work. The top is made of heavy plywood, covered with black linoleum, provided with an aluminum edge that extends above the surface for 0.25 inch (0.6 cm.) and retains mercury spilled or expelled from the apparatus. The legs are made of telescoping steel tubing which make it adjustable in height from about 20 to 31 inches (50 to 79 cm.) and are provided with castors which can be put in or out of operation in an instant by a simple lever device.

Acknowledgment

The author wishes to acknowledge his indebtedness to the management and personnel of the Fisher Scientific Company for the opportunity and coöperation that have made possible the conception and development of the unitized gas-analysis apparatus.

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Extraction of Triethanolamine Oleate from Aqueous Solution

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In the extraction of oil from a soap and oil emulsion, irregular results obtained indicated some abnormality. Further investigation showed that the soap was triethanolamine oleate and that the variable results were due to decomposition of the soap in extraction. Such decomposition is not unexpected, since triethanolamine oleate is a salt of a weak acid and a weak base. The extractions were carried out with ethyl ether and all results were higher than anticipated. The acidity of the extracted material proved to be higher than normal for the type of oil being extracted.

The importance of this behavior is increased by the widespread technical application of triethanolamine oleate as an emulsifying agent and for other purposes. Normally, soaps other than those of abietic acid are not decomposed by extraction of an aqueous solution with ethyl ether. This method of separation of oils, etc., from soap solutions is therefore widely used.

The tentative explanation reached was that triethanolamine oleate was giving up oleic acid because of its instability. To verify this, a 10 per cent neutral triethanolamine oleate solution was extracted with ethyl ether under conditions normal for extraction of soap. A recovery of 85 per cent of the oleic acid present was obtained and the composition of the extract confirmed by titration.

To express this phenomenon quantitatively, a series of experiments was carried out in which triethanolamine oleate was produced in solution alone, in the presence of excess triethanolamine, and in the presence of excess oleic acid. In preparing these solutions, commercial triethanolamine and commercial oleic acid (olive elaine) were titrated and then combined in proportions to give the solutions outlined in Table I.

The extractions were carried out as follows:

A 200-cc. portion of the soap solution was extracted with 3 successive 50-cc. portions of ethyl ether. In each case shaking was carried out for approximately 2 minutes under similar conditions by the same chemist. The composite ether extractions were washed 3 times with 20-cc. portions of water. The ether was then evaporated, and the extract weighed, dissolved in alcohol, and titrated with 0.5 *N* sodium hydroxide. From this titration the amount of oleic acid extracted from the triethanolamine oleate was calculated to terms of percentage. In the case of experiments 3 and 6 the excess of oleic acid was allowed for before this calculation.

The results are summarized in Table I. The original commercial oleic acid contained 97.25 per cent of oleic acid as oleic acid. The acidity of the extract varies from 95.0 to 97.0 per cent by weight, and is highest in the experiments where recovery of the oleic acid was most complete.

More dilute solutions give a more nearly quantitative extraction. A determination of nitrogen on the extract from experiment 1 showed that less than 0.1 per cent of the triethanolamine had been extracted with the oleic acid. Table I indicates the possibility that all of the oleic acid could be recovered by further extractions. The results of 6 extractions instead of 3 showed recoveries as follows: Experiment 1, 76.32 per cent; experiment 4, 93.73 per cent; experiment 6, 81.84 per cent. This indicates that further extraction may approach 100 per cent of the oleic acid present, particularly in dilute solution.

It is to be concluded that normal conditions of separation of oils from soap solutions, in which the soap is triethanolamine oleate, will not apply and that either prolonged extraction with correction for the free fatty acid content is necessary, or that, preferably, a method other than extraction from aqueous solution without acidifying should be used.

Table I. Oleic Acid Extracted from Triethanolamine Oleate Solutions

Experiment	Concentration of Triethanolamine Oleate	Excess Triethanolamine	Excess Oleic Acid	Combined Oleic Acid Present	Weight of Extract	Pure Oleic Acid by Titration, Corrected for Free Oleic Acid	Oleic Acid Extracted, Corrected for Free Oleic Acid	Commercial Oleic Acid Recovered
	M	*M*	*M*	*Grams*	*Grams*	*Grams*	%	%
1	0.1	..	..	5.808	3.4702	3.3050	95.2	58.5
2	0.1	0.05	..	5.808	2.4746	2.3500	95.0	41.7
3	0.1	..	0.05	5.808	6.1986	2.8910	95.4	54.7
4	0.01	..	..	0.5808	0.4265	0.4135	97.0	73.2
5	0.01	0.05	..	0.5808	0.4916	0.4746	96.6	84.0
6	0.01	..	0.05	0.5808	0.6900	0.2660	97.0	68.5

Received August 26, 1933

Conditions to Preserve Publications. Light, adverse temperature and humidity, acid pollution of the air, and low-grade paper appear to be the main deteriorative agents to be guarded against in libraries and other book depositories, according to a report prepared by the Bureau of Standards.

Sulfur dioxide gas is a potential destroyer of all classes of paper, but tests demonstrated that this condition can be completely removed by washing the air with alkaline wash water. The destructive effect of light is emphasized. The removal of dust and the maintenance of a medium degree of temperature and humidity are recommended. Extensive tests of old newspapers showed that many made from crude fibers such as ground wood were badly deteriorated, whereas papers composed of chemically purified fibers were found to be in good condition.

Glass and Other Electrodes for Measuring pH Values of Very Dilute Buffers and of Distilled Water

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In the electrometric measurement of the pH values of buffered solutions more dilute than 0.0001 *M* by means of quinhydrone and hydrogen electrodes the resistance of the solution, escape of carbon dioxide, acid properties of the quinhydrone, and polarization of the electrodes are so disturbing that the e. m. f. readings may vary as much as 5 to 30 millivolts or 0.1 to 0.5 pH unit. The isohydric indicator technic (*1*) is apparently applicable within 0.1 pH to such solutions and distilled water, but has not heretofore been compared with a reliable e. m. f. method. By adding Varley shunts to a modification of the vacuum tube potentiometer used by Partridge (*5*), keeping the grid attached to the circuit when balancing it, and using a Thompson (*2, 3, 4, 7*) glass electrode, e. m. f. readings can be made within 0.1 to 2.0 millivolts on weakly buffered solutions and distilled water, and the pH values agree with those obtained by the isohydric indicator method. This combination is also suitable for measuring the pH of solutions containing active oxidizing or reducing agents, such as chlorine or tannins (*6, 8*) where the hydrogen and quinhydrone electrodes and indicator methods might fail.

Figure 1 shows a diagram of the circuit used with a special Duovac triode tube. Recent work by the authors shows that the F. P. 54 G. E. tube is especially good with this circuit.

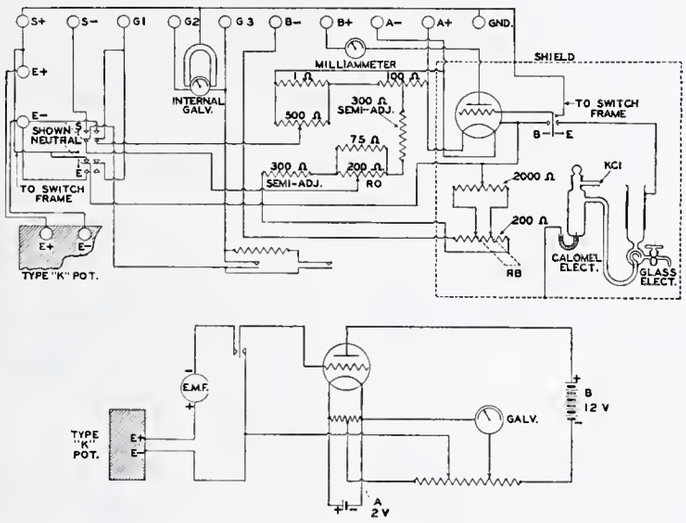

Figure 1. Wiring Diagram of Glass Electrode–Potentiometer System

Upper, circuit as modified in this work
Lower, schematic Partridge circuit

The sensitivity of this modified equipment with the Leeds and Northrup Type K potentiometer and 2500-e galvanometer and the Thompson glass electrode of about 60 megohms resistance, made from Corning No. 015 glass is about 0.004 millivolt per mm. scale division with 0.001 *M* sodium, acid phthalate (designated NaHPh in Table I), 0.007 millivolt with 0.0001 *M* solution and 1 millivolt for double-distilled water. Standard cells can be checked to within 0.1 millivolt. With the Thompson glass electrode the readings are easily made to within 0.1 millivolt, are reproducible with double-distilled water to within 2 or 3 millivolts, and become better as the buffer concentration increases.

Table I gives some illustrative pH data on dilute solutions. The results show that the hydrogen electrode (1 × 1 cm. gold covered with palladium sponge) gives drifting readings in very dilute solutions, especially tap water and distilled water containing traces of carbon dioxide. The quinhydrone electrode (1 × 1 cm. gold) gives e. m. f. values which decrease steadily for 20 to 30 minutes as the weakly acid solid quinhydrone dissolves. Chlorine attacks the quinhydrone and alters the e. m. f. values. The glass electrode and isohydric indicator methods give approximately the same pH values in very dilute buffers and distilled water. In general, either method is satisfactory for such solutions. For other samples which are colored, turbid, or possess oxidizing or reducing properties a glass electrode is, of course, to be preferred.

Table I. pH Values of Solutions of Various Concentrations Obtained by Different Methods

	Hydrogen Electrode	Quinhydrone Electrode	Glass Electrode	Isohydric Indicator Method
0.1 *M* NaHPh	3.93	3.93	3.92	3.90
0.01 *M* NaHPh	4.05	4.06	4.04	4.05
0.001 *M* NaHPh	4.34	4.37 to 4.33	4.35	4.30
0.0001 *M* NaHPh	4.85	4.82 to 4.72	4.84	4.90
0.00001 *M* NaHPh	5.68 to 5.95	5.34 to 5.20	5.61	5.70
Tap water	8.42 to 8.98	7.11	7.58	7.70
Boiler water	11.74	..[a]	11.52	11.70
Double-distilled water	6.18 to 7.66	6.05 to 5.71	6.57	6.50
Leather extract	5.28	5.40	5.25	..[b]
0.01 *M* buffer containing 0.07 gram of chlorine per liter[c]	4.59	4.66	4.72	..[d]
0.01 *M* buffer containing 1 gram of chlorine per liter[e]	..[f]	0.20	1.90	..[d]

[a] Solution too alkaline for quinhydrone electrode.
[b] Solution too deeply colored for indicator method.
[c] Solution prepared by diluting 50 ml. of 0.05 *M* KHPh-NaOH solution (pH = 4.80) and 5 ml. of saturated chlorine water (pH = 1.71) to 250 ml.
[d] Indicator faded quickly.
[e] Solution prepared by passing chlorine gas into 0.01 *M* KHPh-NaOH solution (pH = 4.80).
[f] Solution removed palladium sponge from electrode.

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An Automatic, Modified Falling-Sphere Viscometer

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An automatic, modified falling-sphere type of viscometer for very viscous liquids has been developed and put into practical use as a factory-control instrument. The instrument is shown to give reproducible results for rubber cements and for petroleum products. In addition, it is demonstrated that viscosities obtained on this instrument are nearly proportional to absolute viscosities over a very wide range.

An instrument, suitable for factory use, was needed for the measurement of the consistency of rubber cements The principal requirements were that it should indicate the consistency of a cement automatically, yield results fairly rapidly, be convenient to operate, and be of rugged construction. It was thought that the falling-sphere type of viscometer was more suitable than any of the other types, and accordingly means were considered for making the falling-sphere viscometer automatically indicating.

Methods Considered

High Frequency. This method is described by Broome and Thomas (*1*), by Symmes and Lantz (*11*), and by Moore and Cuthbertson (*8*), who used a vacuum-tube oscillator, in an appropriate circuit. The presence of a steel ball at a point is determined by the operator by the change of a beat-frequency note heard in headphones. The disadvantage of this method is that the rate of change of the beat-frequency note is a function of the velocity of the ball. Thus the precise time at which the note becomes inaudible is a matter of the personal judgment of the operator.

Photoelectric. An excellent apparatus of this type is described by Jones and Talley (*4*). Photoelectric methods are inconveniently complicated when the sample is itself opaque, as is often the case with rubber cements.

Electromagnetic. Consideration was given to a method of electromagnetically detecting the presence of a steel ball at a point in the liquid Laboratory experiments, not described herein, showed that the method was impractical.

Contacts. If the viscous liquid is an electrical insulator (as is nearly always the case with rubber cement), and a metallic sphere is used, the timing of the fall of the sphere may be accomplished by allowing it to come into contact with a pair of mutually insulated electrodes at the upper end of the column of liquid, and into contact with another pair of electrodes at the lower end. The short-circuiting of the electrodes by the sphere may be utilized to operate some external timing device. This apparatus is very much simpler than any of the others considered and, in addition, can be more ruggedly constructed. For these reasons it was decided to develop this type of automatic instrument. The method is not new. Robinson (*9*), in 1929, patented a viscometer for nontransparent liquids. The patent describes a falling-sphere method in which the arrival of the sphere at the bottom of the column of liquid is indicated by an electric light, the circuit to which is closed by connections operated by the sphere. The patent does not cover automatic timing.

Development of Apparatus

Great difficulty was experienced in obtaining a type of electrode that would make a definite electrical contact with a hardened steel ball when both were immersed in rubber cement. Steel balls were chosen for the reasons listed by Sheppard (*10*), and Gibson and Jacobs (*2*). Obviously the contact area between a smooth, hardened sphere and a metal electrode is very small, and consequently of high resistance. The difficulty was enhanced by the fact that the steel balls did not always fall vertically in very viscous cements and, therefore, sometimes alighted on only one electrode. In some instances the ball took as long a period of time to "settle" on the second electrode after making contact with the first, as it took to fall through the entire column of cement to the first electrode.

Several unsuccessful types of electrodes were tried before it was decided that, in order to attain absolute reliability of operation, it would be necessary to guide the ball along a definite path towards a pair of definite points on the two electrodes. It was realized that if the fall of the ball was restricted or constrained by guides it would be impossible to express the velocity of the ball by Stokes' law, and that Ladenburg's correction factor for wall effect would not apply. For routine factory-control use, however, it was considered more important for the automatic instrument to be reliable in operation, than for the velocity of the ball to be expressible according to a known law.

Apparatus and Method of Use

The apparatus finally adopted may be described briefly as an inclined guide immersed in the liquid to be tested. The ball is released from an electromagnetic member immersed a short distance beneath the surface of the sample, and at the same instant an electric clock is automatically started. The ball moves down the guide for a fixed distance in the liquid until it comes into contact with a sharp-edged electrode (the guide itself being the other electrode). When the ball strikes the lower electrode, the electric clock is automatically stopped, and the reading of the clock is a measure of the viscosity of the liquid.

The complete apparatus, as built and put into use in the factory, and the method of operation, will be understood most easily by reference to the schematic diagram (Figure 1).

A glass or metal tube, sealed at the lower end by any suitable means, is filled with about 350 cc. of the cement to be tested. Into this tube of cement is inserted a rigid steel guide, a cross section of which is shown in Figure 2, which is firmly held in a clamp at an angle of 75° to the horizontal. Integral with the guide at its upper end is an iron-core electromagnet to which is attached a steel pole-piece. The electromagnet and pole-piece are electrically insulated from the guide. A steel ball (9.525 mm., 0.375 inch, diameter) is allowed to fall into the liquid through a hole (11.1 mm., 0.44 inch, diameter) in the steel pole-piece. The ball rolls into the starting position (1), at the tip of the pole-piece, about 25 mm. (1 inch) beneath the surface of the rubber cement, and is held there by the alternating magnetic flux passing

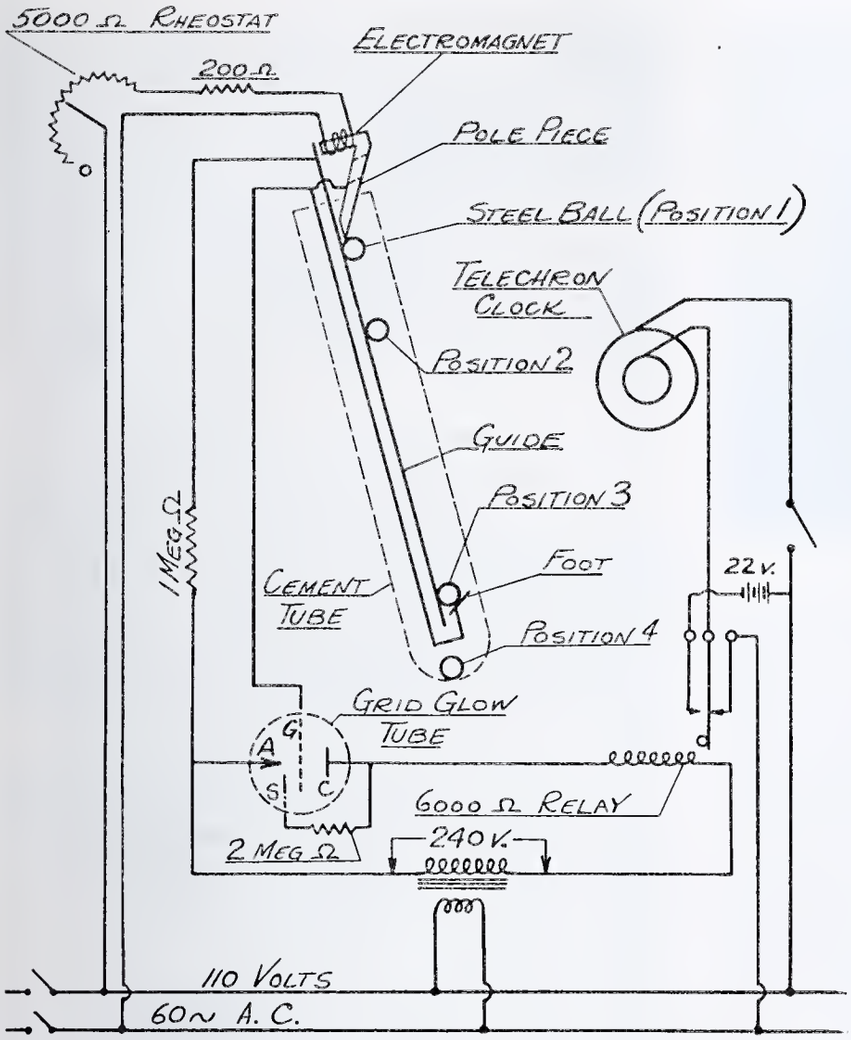

FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS

between the pole-piece and the steel guide. This magnetic flux is induced by the electromagnet which is excited by alternating current from the 110-volt line.

The pole-piece is grooved on its inner surface, so that the ball is always guided to the same relative position between the pole-piece and the guide. The inner surface of the tip of the pole-piece is of semicircular cross section, so that the ball is always held in the same lateral position relative to the pole-piece and the guide. The level of the ball (at position 1) is determined by the location of the greatest flux density between the pole-piece and the guide. This position does not vary by an amount sufficient to be detected, either by observation or by its effect on the results obtained.

When held in this position, the ball is in electrical contact with both the pole-piece and the guide, and forms part of the circuit between the anode and the grid of a glow-discharge tube. [For a complete theoretical and practical discussion of this tube, known commercially as a Grid Glow tube, type DKU-618, the reader is referred to articles by Knowles and Sashoff (*6*) and Knowles (*5*).] When connected as shown in Figure 1, the anode-cathode circuit is nonconducting if the combined resistance of the parallel paths between the guide and the foot and the guide and the pole-piece is more than 8 megohms. This condition obtains when the surrounding medium is an ordinary commercial rubber cement, or a petroleum lubricating oil. When either of the two parallel paths referred to above has a resistance less than 8 megohms, as when the steel ball connects the guide and the pole-piece, the tube is in a state of discharge—that is, the anode-cathode circuit will pass a uni-directional, pulsating current (15 milliamperes maximum average). This current may be used to energize a relay. The current passing through the grid-anode circuit is at all times very small, the high limiting resistance (1 megohm) always being in the circuit, so that the making and breaking of the grid-anode circuit by the sphere is accompanied by the minimum of sparking.

Referring again to Figure 1, it will be seen that when the ball is in position 1, touching both the guide and the pole-piece, the Grid Glow tube is in a state of discharge, the relay coil is energized and the Telechron clock is prevented from starting. The clock switch, which previously has been open, is now closed. The steel sphere is now ready to be released for a viscosity determination. The resistance of the rheostat is increased until the current passing through the electromagnet is sufficiently low to allow the ball to fall away from the pole-piece under the action of gravity. At the instant the contact between the ball and the pole-piece is broken, the resistance of the grid-anode circuit is increased by several megohms and the anode-cathode circuit becomes nonconducting. The relay is thus deënergized, and allows the clock contact to close. The 110-volt circuit is thus completed to the Telechron clock, which, being a self-starting synchronous motor, commences to time the fall of the steel ball. The breaking of the contact between the steel ball and the pole-piece, and the starting of the clock occur practically simultaneously. The steel ball now moves down the guide (position 2). This guide (Figure 2) is inclined at an angle of 75° from the horizontal. This particular angle was chosen because it is large enough to be quite positive in its guiding effect upon the ball. The surfaces of the steel guide, down which the ball moves, are highly polished, so that the velocity of the ball will be mainly dependent upon the consistency of the rubber cement being tested.

The distance along the guide from the pole-piece to the foot is approximately 305 mm. (12 inches). This distance was chosen for practical reasons. It was found to be long enough to give a suitable spread in results when used with a

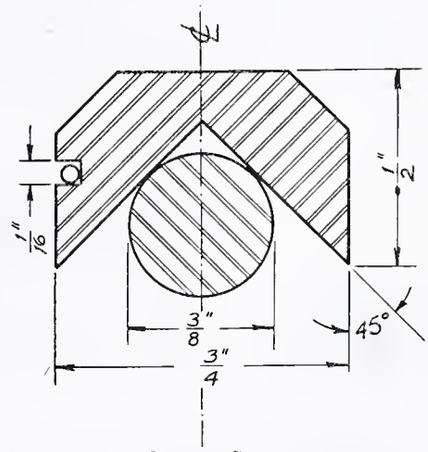

FIGURE 2. CROSS SECTION THROUGH STEEL GUIDE AND SPHERE

ball of 9.525 mm. (0.375 inch) diameter, which is a convenient size to handle. The steel foot is rigidly connected to, but electrically insulated from, the guide. The foot is electrically connected to the pole-piece by means of an insulated wire laid in a groove in the side of the guide. The wire insulation is impregnated with Bakelite varnish, and

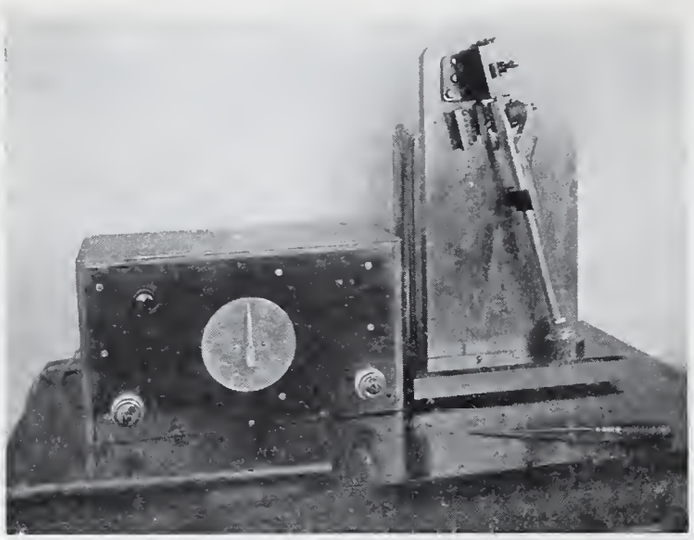

Figure 3. Apparatus Ready for Use

the whole is baked solidly in the groove. At the instant the ball touches the foot (position 3) electrical contact is made, and since the ball is already touching the guide, the resistance of the grid-anode circuit is again decreased to a value less than 8 megohms. The resulting anode-cathode current, or glow discharge, energizes the relay, which then opens the 110-volt line to the Telechron clock. At the same instant as the 110-volt alternating current line is opened, the 22.5-volt direct current line to the Telechron clock is closed, so that the clock is instantly stopped. Without this impressed direct current voltage, the hand of the clock would run for approximately half a second after the current was turned off, on account of the momentum of the moving parts. The reading of the clock in seconds is recorded as a measure of the consistency of the cement. To make a check run using the same sample of cement, it is necessary only to allow the ball to fall off the foot (by tipping the guide sideways), and to proceed as before, using another ball. In order to determine the consistency of another sample of cement, it is necessary to clean both the tube and the guide. After the guide is removed from the tube, the cement adhering to the slide is allowed to dry until it can be peeled off, or else it is washed off with solvent before drying. The tube holding the cement must also be cleaned in a similar manner before it is again filled with a fresh sample of cement. In factory-control work it is advantageous to have several guide assemblies and tubes on hand, so that the cleaning of these parts will not retard the routine testing.

Table I. Reproducibility of Results Using Petroleum Products

	Petroleum Oil Used		
	Medium-heavy motor oil	600 W cylinder oil	Asphaltic base petroleum residue
Number of determinations	15	7	3
Average time, seconds	2.5	5.9	1110
Mean deviation, seconds	0.03	0.16	12
Mean deviation, per cent	1.3	2.7	1.08
Maximum deviation, seconds	0.2	0.3	17
Maximum deviation, per cent	8.0	5.1	1.5
Temperature of oil, ° C.	27	31.5	31.5

Figures 3 and 4 are photographs of the actual apparatus. For convenience in operation, the apparatus is divided into two parts; on the right is shown the wooden stand supporting the clamp, guide, and cement tube. In the cabinet at the left is the auxiliary electrical apparatus including the Telechron clock, relay, and Grid Glow tube. In the top of the cabinet may be seen a small window. Immediately beneath this window is the glow-discharge tube (Figure 4). This window is furnished to enable the operator to see at a glance the condition of the Grid Glow tube, and from it the position of the steel ball. When the operator drops the steel ball through the hole in the pole-piece into a viscous opaque cement he cannot determine visually when the ball is in place at the tip of the pole-piece. However, before the ball is in place the grid-anode circuit is "open," and hence the Grid Glow tube is nonconducting and glows only feebly. As soon as the ball comes in contact with the steel guide and the tip of the pole-piece, the grid-anode circuit is "closed," the Grid Glow tube becomes conductive, and a bright red glow discharge may be seen in the tube. Thus the operator is informed immediately that the ball is in place and ready for a run.

Reproducibility of Results

As a rapid means of determining whether or not the automatic viscometer gives reproducible results, the instrument was used for determining the viscosity of three petroleum products. Each experiment consisted of running consecutively several steel balls through the same tube of oil. The consecutive runs were made as rapidly as possible, so that the temperature of the sample, which was not artificially controlled, would not vary appreciably. The results, summarized in Table I, show that the instrument is reliable and accurate.

Considering the fact that the instrument was designed for the measurement of the consistencies of production rubber cements, which have high viscosities (20 to 500 seconds on the automatic viscometer), it is worthy of note that it gives exceptionally reproducible results for viscosities as low as 2.5 seconds, as is shown by the data for the medium-heavy motor oil.

As a further and more appropriate check on the ability of the instrument to give reproducible results, three rubber cements having a wide range of consistencies were tested in the automatic instrument. One 5-gallon sample of each cement was taken from a large factory batch. From each 5-gallon sample the viscometer tube was filled several times, and only one test was made on each tube of cement. The

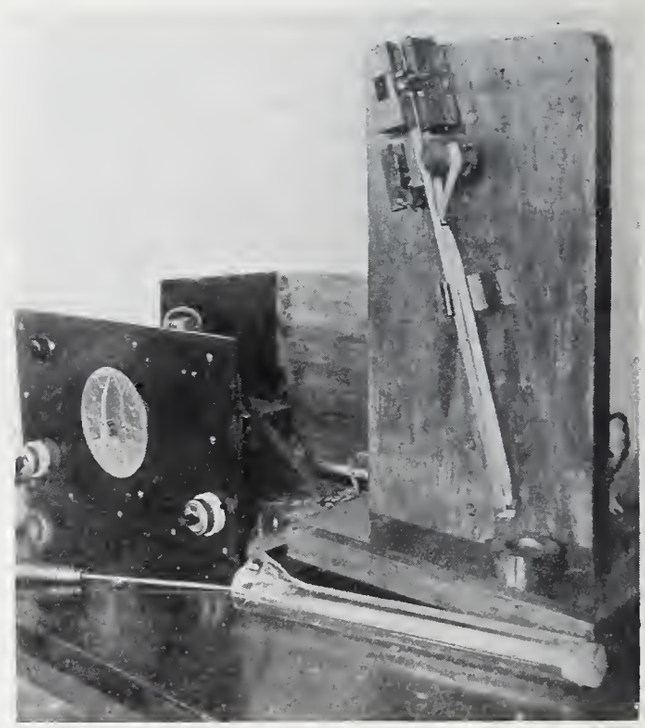

Figure 4. Apparatus

Cover of cabinet removed, cement tube removed to show steel guide and steel ball at tip of pole-piece.

tests were made at room temperatures. The 5-gallon containers were kept tightly sealed during the intervals between the withdrawal of consecutive samples, so that there would be no unnecessary loss of solvent by evaporation. In order to demonstrate that the accuracy of the results obtained on this instrument does not depend upon the skill of the operator, the tests on cement K were run by two operators.

Table II. Reproducibility of Results Using Rubber Cements

	Cement K[a]	Cement L[b]	Cement M[c]
Number of determinations	19	6	5
Average time, seconds	26	64.2	291
Mean deviation, seconds	0.7	1.15	19
Mean deviation, per cent	2.7	1.8	6.5
Maximum deviation, seconds	2.0	2.8	34
Maximum deviation, per cent	7.7	4.35	11.7
Average temperature, ° C.	28.5	26.5	30

[a] 5% milled smoked sheet, gasoline, iron oxide, zinc oxide.
[b] 8% first latex crepe in gasoline.
[c] 10% first latex crepe in gasoline.

The results shown in Table II are indicative of the reliability of the instrument in giving reproducible measurements of the consistency of rubber cements. The maximum deviation shown is believed to be within the limits of variability of the consistency of a rubber cement occasioned by evaporation of solvent, change of temperature, and nonhomogeneity.

A considerable amount of time (5 to 10 minutes) is required for emptying, cleaning, and refilling the apparatus with a fresh sample for the purpose of making a check determination. Hence an experiment was run to ascertain whether or not it would be possible to make check determinations by running consecutive steel balls in the same tube of rubber cement. For this experiment, eight different rubber cements were chosen, covering a wide range of consistencies. Several steel balls were run through the same tube of each of the eight cements. The balls for the consecutive tests were each loaded into the instrument as rapidly as possible after the preceding ball had been removed from the foot, so that the consistency of the rubber cement in the tube would have very little chance to change, between runs, by evaporation of the solvent.

The results obtained in this experiment are shown graphically in Figure 5. Three of the rubber cements gave reasonably constant values of consistency as succeeding balls were used. The other five cements, however, yielded remarkably variable results, the general tendency being for the apparent consistency to increase steadily up to some maximum, then to decrease suddenly, only to increase again to some still higher maximum consistency as succeeding balls were allowed to fall through the cement. It will be noticed that the three rubber cements of low consistency gave constant results and that the five of higher consistency gave variable results. No investigation was carried out for the purpose of determining the cause of the increase in consistency. It is thought, however, that the increase is evidence of a grain effect in the rubber cement brought about by the mechanical working of the cement by the successive steel balls as they fall along the same path. Obviously, it is impossible, with cements showing this effect, to obtain check results by using successive balls in the same tube of rubber cement.

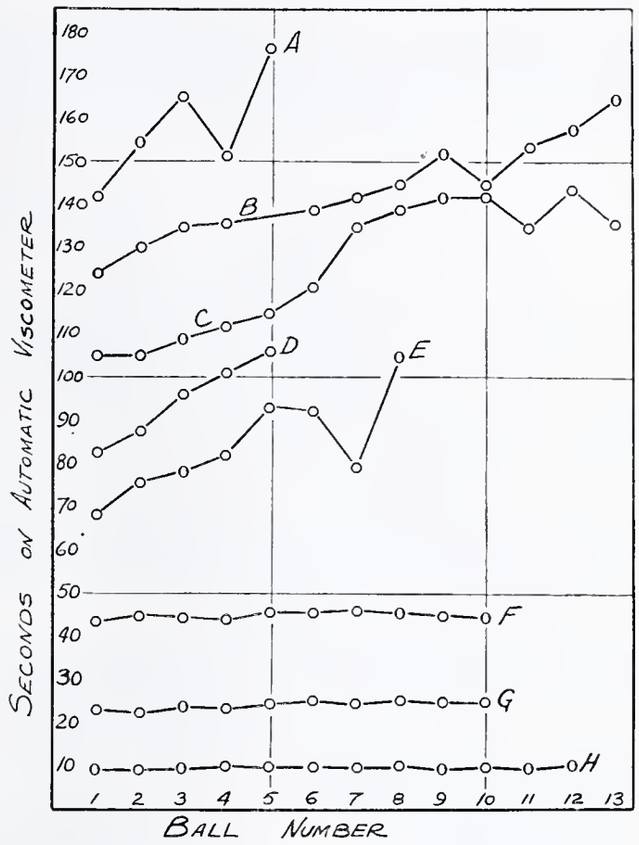

Figure 5. Effect of Repeated Tests on Apparent Consistency of Same Samples of Rubber Cement

A. 8 per cent first latex crepe in gasoline
B, C, E. 7 per cent first latex crepe in gasoline
D. 10 per cent first latex crepe in gasoline
F. 5 per cent milled smoked sheet in gasoline; iron oxide, zinc oxide
G. 5 per cent milled smoked sheet in benzene and gasoline
H. 4 per cent milled smoked sheet in benzene and gasoline
The seven batches of rubber used in these cements were not necessarily milled for the same length of time.

Relationship between Automatic Viscometer Seconds and Absolute Viscosities

Some question arose as to whether the automatic instrument would yield values of relative viscosity which are proportional to absolute viscosities. To settle this debatable point, three true liquids, having a wide range of viscosities, were chosen for test. These were run both in a viscometer of the usual falling-ball type, and in the automatic instrument. The three liquids chosen were castor oil, corn sirup, and Venice turpentine. All the measurements in this experiment were made at room temperatures, 24° to 25.5° C. The absolute viscosity of the castor oil was determined as 7.15 poises, by calculation from the Saybolt viscosity and the specific gravity, using the formula given by Herschel (*3*).

The same sample of castor oil was then used as a calibrating liquid for the usual type of falling-ball viscometer—that is, the castor oil was used for the purpose of obtaining the instrument constant, K_1 in the formula:

$$\eta = K_1 (d_1 - d_2)\, t_1 \qquad (1)$$

where η = absolute viscosity in poises

$$K_1 = \frac{2\, gr^2}{9l\left(1 + 2.4\,\frac{r}{\rho}\right)\left(1 + 3.3\,\frac{r}{h}\right)} \qquad (2)$$

d_1 = density of falling sphere
d_2 = density of the liquid
t_1 = time of fall in seconds in falling-ball viscometer
r = radius of the sphere in cm.
ρ = radius of the cylinder in cm.
l = distance in cm. through which the sphere falls vertically in the liquid
h = height of the liquid in cm.

The value of K_1 is a constant for constant values of r, ρ, l, and h. It is, of course, merely a convenient grouping of various constants of Stokes' law and Ladenburg's correction formula (*7*). The value of K_1 for the particular falling-ball viscometer used was 0.455. Substituting this in Equation 1, and using the values of t_1 and d_2 obtained for the samples of corn sirup and Venice turpentine, the absolute viscosities of these two liquids were found to be 19.9 poises and 1450 poises, respectively.

The three liquids were then run in the automatic instrument. Here, again, the castor oil was used as a calibrating liquid, and from the time in seconds obtained, and the specific gravities of the steel ball and castor oil, an instrument constant K_2 was calculated thus:

$$K_2 = \frac{\eta}{(d_1 - d_2)\, t_2} \qquad (3)$$

Then

$$K_2 = \frac{7.15}{(7.79 - 0.958)\, 4.72} = 0.222$$

It is understood, of course, that K_2 is not the same function of r, ρ, l, and h as is K_1, for it is impossible to apply Ladenburg's corrections to the automatic instrument. The value of 0.222 obtained for K_2 in Equation 3 was substituted in the formula

$$\eta = K_2\, (d_1 - d_2)\, t_2 \qquad (4)$$

for the determination of the absolute viscosities of the samples of corn sirup and Venice turpentine. In 4 the value of t_2 is the time obtained on the automatic instrument. The summarized results are shown in Table III.

Table III. Comparison of Absolute Viscosities Obtained on Falling-Ball Viscometer and Automatic Viscometer

	Castor Oil	Corn Sirup	Venice Turpentine
1 Automatic viscometer, seconds	4.7[a]	15.6[b]	1135[c]
2 Absolute viscosities calculated from automatic viscometer times, poises	7.15	22.2	1710
3 Absolute viscosities obtained from falling-ball viscometer, poises	7.15	19.9	1450
4 Ratio between 2 and 3	1	1.115	1.180

[a] Mean of 9 determinations.
[b] Mean of 5 determinations.
[c] Mean of 3 determinations.

The results in Table III show that over a wide range of viscosities the automatic viscometer gives values of relative viscosity which, when corrected for the specific gravity of the liquid, are nearly proportional to absolute viscosity. The 18 per cent error in the absolute viscosity of Venice turpentine and the 11.5 per cent error in the viscosity of corn sirup are no greater than should be expected when it is considered that Equation 3 applies strictly to only true falling-sphere viscometers, in which r is small with respect to ρ, and does not apply to the more complicated case of a ball rolling down an inclined V-shaped guide, as was assumed in Equations 3 and 4.

Temperature Corrections

For factory-control work, where rapidity in obtaining results is an important factor in the use of any instrument, it is not practical to measure the consistency of a rubber cement at a standard temperature, because of the difficulty of bringing the cement to that standard temperature within a reasonable time. For this reason, the automatic viscometer, instead of being equipped with an elaborate temperature control, was furnished to the factory operators with a temperature-correction table applicable to rubber cements of all consistencies actually met with in practice, and covering a range of temperatures greater than that normally encountered in the cement-house.

Conclusion

The automatic viscometer described in this paper is a simple, rugged instrument suitable for factory-control work where reliability of operation is of prime importance. It is not claimed that the instrument will give results with as high a degree of accuracy as certain other automatic viscometers, such as the one described by Jones and Talley (*4*), or as the manually operated Saybolt, Ostwald, or straight falling-sphere viscometers provided with thermostatically controlled constant-temperature baths. However, it is better suited than other viscometers to the automatic measurement of the consistency of very viscous rubber cements, whether they are transparent or opaque. The instrument will yield results which are within the limits of variability encountered in rubber cement itself, as the data in Table II show. It will yield results quickly, actual times in seconds on the instrument being approximately equivalent to poises when the specific gravity of the liquid is about 1 and steel balls of 9.525 mm. (0.375 inch) diameter are used. The instrument requires only a small amount (350 cc.) of cement for one determination, and its operation requires no greater skill than the ability to turn three switches in correct sequence. The particular apparatus shown in Figures 3 and 4 has been used by factory operators over a period of 6 months at the time of writing.

Acknowledgment

The author thanks Norris Johnston and N. A. Shepard for their many valuable criticisms and suggestions throughout the course of this work.

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Cleaning Platinum Wire for Flame Tests

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The usefulness of potassium acid sulfate for removing persistent deposits from a platinum test wire seems to have been overlooked in textbooks on qualitative analysis, in spite of the fact that this very effective flux is commonly recommended for cleaning platinum vessels. In the hands of a student in qualitative analysis a platinum wire occasionally acquires a deposit which volatilizes sufficiently to contaminate flame tests, but which is removed with difficulty by hydrochloric acid and heat. In such cases it is more effective to use potassium acid sulfate. A coating of potassium acid sulfate is picked up by drawing the hot wire across a piece of the solid salt. On passing the wire slowly through a flame, the bead of potassium pyrosulfate which forms travels along the wire, dissolving the contaminating deposits. When cool, the bead is readily dislodged. Any small residue of pyrosulfate dissolves at once in water, while the last traces are usually removed by a single moistening with concentrated hydrochloric acid, followed by heating. The clean, bright platinum resulting imparts no color to the flame.

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Capillary Penetration of Fibrous Materials

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This paper is a study of the penetration of liquids into porous materials, with special reference to the use of capillary rise in strips of fibrous materials as a test method for the evaluation of the penetration tension of the liquid-solid system (the penetration tension being the product of the surface tension and the cosine of the contact angle). It is shown theoretically that the rate of rise, dh/dt, varies linearly with the reciprocal of the height of rise, $1/h$, and that the slope of the straight line obtained by a plot of these quantities is proportional to γ/η, where γ is the penetration tension and η the viscosity of the liquid. The proportionality constant is shown to be dependent not merely on the average pore size, but on the extent of the range of pore sizes represented. Using a single solid medium, therefore, relative values of the penetration tension for various liquids may readily be determined. Experimental data supporting the theory are presented.

NUMEROUS industrial processes consist essentially in the penetration of fibrous materials by liquids. As examples of such processes may be cited the treatment of wood with preservative substances, the dyeing of textiles, and the impregnation of paper, wall board, and felt with materials which increase their resistance to heat or moisture, or which improve their properties as electrical insulators. Any understanding of these processes must rest upon a knowledge of the dynamics of capillary penetration into such materials. Moreover, it is known that the interfacial forces which cause such penetration are related to the adhesion between the penetrating material and the medium impregnated. Hence the determination of the forces effective in impregnation should afford information bearing on the nature and extent of the adhesion obtaining in the impregnated material.

The experimental investigation of the capillary penetration of fibrous materials presents a number of difficulties. Capillary forces are commonly investigated by means of the rise in capillary tubes or the spreading on plane surfaces. These methods cannot be applied to fibrous materials. For cellulose materials, use might be made of tubes or plates of regenerated cellulose, but these might well exhibit different interfacial forces with a given liquid than would the parent substance. In these laboratories, attempts have been made to use the method of Bartell and Osterhof (*1*), in which there is measured the pressure required to prevent the penetration of a liquid into a porous material packed in a cell. These attempts have not been successful, presumably because of the difficulty of packing fibrous materials in the cell in such a way as to assure uniform pore size.

It is, however, possible to study the capillary penetration of fibrous materials directly, in some cases, by observing the rate at which the liquid will rise in a strip of the material when dipped in the liquid. While this is a fairly common qualitative test, it does not appear to have been employed for the quantitative determination of interfacial forces. By a slight extension of available theory, however, it has been found possible so to analyze the data from a test of this type as to obtain quantitatively comparative results. Experimentally, the method is attractive, as it is simple and rapid and may be readily applied under conditions affording a relatively high degree of reproducibility.

THEORY OF WETTING

In order to present the theory applying to the method, it will be convenient to review briefly the concepts involved in the general theory of capillary action in the form in which they have been presented by recent writers (*6*, *7*). When a liquid spreads over a plane surface, each unit of area covered involves the loss of the energy (S_{SG}) required to form unit area of solid-gas interface, and the addition of the energy (S_{SL}) required to form unit area of solid-liquid interface, and of the energy (S_{LG}) required to form unit area of liquid-gas interface. The increase in free energy involved in spreading over unit area is therefore

$$\Delta F = S_{SL} - S_{SG} + S_{LG} \qquad (1)$$

S_{LG} is numerically equal to the surface tension of the liquid. The quantity $S_{SG} - S_{SL}$, a constant of the solid-liquid pair, is the Freundlich "adhesion tension," A_{SL}. If the ratio of the adhesion tension to the surface tension for any solid-liquid system is written as K, so that

$$A_{SL} = KS_{LG} \qquad (2)$$

the condition that spreading will occur—i. e., that ΔF in Equation 1 be less than zero—can be written $K > 1$. If this condition does not hold, K being less than unity, the liquid will come to rest with its surface making an angle Θ with the solid surface, such that $\cos \Theta = K$.

The case of capillary rise differs from that of spreading in

that no liquid-gas interface is formed. Hence for each unit area of capillary wall covered, the energy loss is equal to the adhesion tension alone, so that the condition for such rise is merely that $K > 0$, or that $\Theta < \frac{\pi}{2}$. The effective force per unit length causing capillary rise will be here termed the penetration tension, and denoted by the symbol γ. The penetration tension is equal to the adhesion tension when the contact angle Θ is greater than zero. If $K > 1$, the penetration tension is merely the surface tension (S_{LG}) of the liquid, as this is the greatest force which can act on the periphery of the advancing column. When $K > 1$, the liquid will spread out along the walls of the capillary faster than the column of liquid will advance.

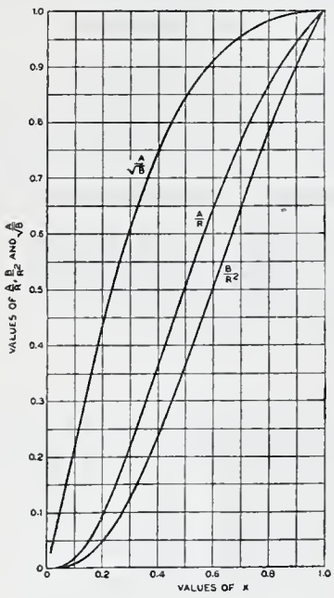

FIGURE 1. A/R, B/R^2, $A/\sqrt{B}$ AS FUNCTIONS OF x FOR UNIFORM DISTRIBUTION OF PORE SIZES

It may be further noted that while A_{SL} cannot be directly measured when $K > 1$, it may be obtained indirectly by measuring the capillary rise of the liquid in a tube containing it and another liquid, immiscible with the first, for which A_{SL} is known (as will be the case if for the second liquid $K < 1$). For at the interface of the two liquids the equilibrium condition gives

$$S_{LL}' \cos \Theta' = S_{SL} - S_{SL}' = A_{SL} - A_{SL}' \qquad (3)$$

where S_{LL}' is the energy per unit area of the interface between the two liquids and Θ' the angle this interface makes with the solid wall.

CAPILLARY PENETRATION

The penetration of liquids into capillary tubes has been considered by Washburn (*9*) and Bosanquet (*2*). The latter's treatment is more complete than the former's, in that inertia effects are considered. These were shown by Washburn to be trivial after the penetration has proceeded a measurable distance, and for small capillaries may be neglected. Taking the simplest case, in which the viscosity of the displaced gas is neglected, the treatment consists simply in substituting the force producing the motion for the total force producing flow in Poiseuille's law. As noted above, the capillary force per unit length of periphery, or penetration tension, will be here written as γ. The total force producing motion is given for a circular capillary by $2\pi R\gamma$, less the hydrostatic head, so that for a vertical capillary

$$\frac{dh}{dt} = \frac{R^2P}{8\eta h} = \frac{1}{8\eta h}(2R\gamma - R^2ghd) \qquad (4)$$

where R is the radius of the capillary, h the height of the column, dh/dt the rate of penetration, g the acceleration due to gravity, and η and d are the viscosity and density of the liquid, respectively. Washburn (*9*) gives an integral of Equation 4, but this is not convenient for comparison with actual data. By evaluating the slopes of tangents drawn to a plot of h versus t, or by means of interpolation formulas, values of dh/dt may be determined, and if these are plotted against $1/h$, a straight line should be obtained, if Equation 4 applies. The validity of this equation, as applied to a single straight capillary, has been confirmed by experiment, as will be shown below.

In a similar manner equations can be derived for the rate of motion in various possible experiments in which one immiscible liquid displaces another in a capillary tube. In such cases the force acting at the interface of the two liquids will be given by $2\pi R\gamma'$, where γ' is the difference $A_{SL} - A_{SL}'$, given by Equation 3.

POROUS PENETRATION

The problem of flow into or through a porous or fibrous medium is obviously more complex than that of flow through a single uniform capillary. The channels in a porous medium will be similar in shape and arrangement to the spaces between spheres piled together, while in a fibrous material they will resemble the spaces within a bundle of cylinders. The liquid flowing at one instant in a large pore space will at the next be divided into streams flowing through smaller spaces, which will unite with each other or with other streams at the next large pore space. The simplest model of these channels that will bear any relation to the facts is one involving a set of capillaries in parallel alternating in series with larger capillaries, each capillary whether small or large varying in radius along its length, and therefore similar in its viscous resistance to a set of shorter capillaries in series.

An exact mathematical treatment for the viscous flow through such an aggregation of channels could be developed only by assuming a specific arrangement of pore spaces. The essential distinction between the flow through such channels and through a group of uniform parallel capillaries, however, can be brought out by considering a hypothetical case in which each channel consists simply of a number of single capillaries in series. This case will differ from the model described in the preceding paragraph only in that each group of small capillaries in series that feed or are fed by larger capillaries will be replaced by single capillaries having the same resistance to viscous flow.

For this hypothetical case, then, it will be assumed that the pores in the medium vary in size in accordance with some distribution function, such that the fraction dN of the total number of pores having a radius lying in the interval from r to $r + dr$ is given by

$$dN = \Phi(r)\, dr \qquad (5)$$

In any single channel, then, the various capillaries in series of which it is constituted will occur with a frequency given by Equation 5. Now the pressure drop per unit length in a uniform capillary is given by Poiseuille's law as

$$\frac{P}{L} = \frac{8\eta}{\pi r^4}\frac{dV}{dt}$$

Evidently the pressure drop through a series of capillaries in series is additive, so that the total pressure drop through a channel of length h is given by

$$\frac{P}{h} = \frac{8\eta}{\pi}\frac{dV}{dt}\int_{-\infty}^{\infty}\frac{\Phi(r)\, dr}{r^4}$$

If the particular channel in question has, at the height h, a radius R, the pressure P effective in producing vertical capillary rise is given by

$$\pi R^2P = 2\pi R\gamma - \pi r^2ghd$$

so that the rate of efflux from this channel at the height h will be

$$\frac{dV}{dt} = \frac{\frac{\pi}{8\eta h}\left[\frac{2\gamma}{R} - hdg\right]}{\int_{-\infty}^{\infty}\frac{\Phi(r)\, dr}{r^4}}$$

The total efflux will be given by adding the efflux from the various channels, and as the radii that these have at any height are distributed in accordance with Equation 5, the total efflux is given by

$$\frac{dV}{dt} = \frac{\frac{\pi}{8\eta h}\left[\int_{-\infty}^{\infty} \frac{2\gamma\,\Phi\,(r)\,dr}{r} - hdg\right]}{\int_{-\infty}^{\infty} \frac{\Phi\,(r)\,dr}{r^4}}$$

Now at any height the rate of rise, dh/dt, will not be uniform, but will vary from channel to channel. If it is assumed, however, that the average distance along a channel from maximum to minimum radii is small, the rate of rise will be apparently uniform, the variations from channel to channel appearing only as minor irregularities in the surface marking the average height attained throughout the medium. This is, indeed, what is actually observed. This approximately uniform rate of rise, dh/dt, can be evaluated by equating the efflux corresponding to a uniform rate in every channel with that given by the preceding equation. It follows that

$$\frac{dV}{dt} = \frac{dh}{dt}\int_{-\infty}^{\infty} \pi\, r^2\, \Phi\,(r)\, dr$$

from which,

$$\frac{dh}{dt} = \frac{\int_{-\infty}^{\infty} \frac{2\gamma\,\Phi\,(r)\,dr}{r} - hdg}{8\eta h \int_{-\infty}^{\infty} r^2\,\Phi\,(r)\,dr \int_{-\infty}^{\infty} \frac{\Phi\,(r)\,dr}{r^4}} \qquad (6)$$

Equation 6 gives the rate of rise in a porous medium having the structure of the hypothetical case considered, in which each channel consists simply of a number of single capillaries in series, or of a single capillary varying in radius along its length. This hypothetical case differs essentially from that obtaining in any actual porous or fibrous medium only in that in the latter each channel will include groups of small capillaries in parallel.

For practical purposes, Equation 6 may be written in the form

$$\frac{dh}{dt} = \frac{A\gamma}{4\eta h} - \frac{Bdg}{8\eta} \qquad (7)$$

where A and B are dependent only on the distribution of pore sizes in the medium, and are therefore constants for a given medium. It follows that the rate of rise, dh/dt, should give a straight line when plotted against $1/h$. Using the same medium, the intercepts of such straight lines, obtained with different liquids, should be proportional to d/η, affording a check on the equation. As the slopes of these straight lines should be proportional to γ/η, relative values of γ can be thus determined.

Before presenting a comparison of experimental data with Equation 7, there will be given a qualitative demonstration of the significance of this equation in so far as the effect of the distribution of pore sizes is concerned. This is readily done by assuming as a simple ideal case that all pore sizes between upper and lower limits are equally frequent, or that the distribution function of Equation 5 has the form

$$\Phi\,(r) = C \text{ for } R_1 < r < R_2$$
$$\Phi\,(r) = 0 \text{ for } r < R_1 \text{ and } r > R_2 \qquad (8)$$

As by definition the integral of Equation 5, $\int_{-\infty}^{\infty} dN$, must be unity, the constant C of Equation 8 must equal $1/(R_2 - R_1)$. Applying to the form of $\Phi\,(r)$ given by Equation 8 the integrations indicated in Equation 6, the constants A and B of Equation 7 are found to have the following values

$$A = \frac{9x^3 \log_e x}{(x-1)\,(x^2+x+1)^2}\,R$$
$$B = \frac{9x^3}{(x^2+x+1)^2}\,R^2$$

where $x = R_1/R_2$ and R_2 is written simply as R. In Figure 1 are plotted as functions of x, the values of A/R and B/R^2 given by these equations. If the values of A and B thus obtained are substituted in Equation 7 and the resulting expression compared with Equation 4, it will be seen that the two expressions differ only in that Equation 7 then involves the functions of x plotted in Figure 1. If x equals unity—i. e., the pore size is constant—the two expressions are identical, as they should be. If x is small, however, corresponding to a wide variation in pore sizes, the two expressions differ in the relative magnitude of their terms.

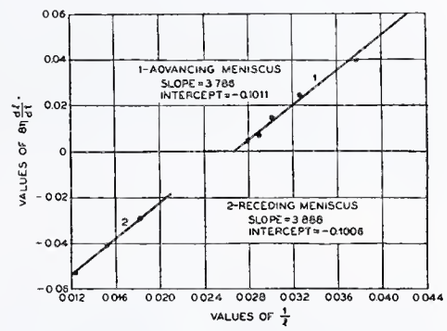

FIGURE 2. $8\eta\, dL/dT$ VS. $1/L$ FOR WATER IN GLASS CAPILLARY

The other quantity, $A/\sqrt{B}$, plotted in Figure 1, is obtained from the expressions given above, and is a function of x only, which can be evaluated from the ratio of the slope of the plot of dh/dt versus $1/h$ to the square root of the intercept, which can be seen from Equation 7 to be equal to

$$\frac{A\gamma}{\sqrt{B}}\sqrt{\frac{1}{2\eta dg}}$$

EXPERIMENTAL: SINGLE UNIFORM CAPILLARY

Experimental confirmation of the expression given above for uniform capillaries is most readily obtained by considering a somewhat more general case; that of a uniform capillary inclined at an angle α to the horizontal, and having a length L_1 dipping below the free surface of the liquid. Paraphrasing the argument used to derive Equation 4, the expression for this more general case can be shown to be

$$\frac{dL}{dt} = \frac{2R\gamma + R^2 L_1 dg \sin\alpha}{8\eta L} - \frac{R^2\, dg \sin\alpha}{8\eta} \qquad (9)$$

where L is the length of tube penetrated.

It follows that a plot of $8\eta \frac{dL}{dt}$ against $\frac{1}{L}$ should be a straight line of intercept $-R^2\, dg \sin\alpha$ and of slope $2R\gamma + R^2 L_1 dg \sin\alpha$. Figure 2, curve 1, shows such a plot of the data for distilled water penetrating a capillary inclined at an angle of 9°22′ to the horizontal. Previous to the test, the capillary had been wet by forcing the liquid back and forth several times. Curve 2 of the same figure shows the data for water in the same capillary when flowing back toward the equilibrium position from a greater height. Calculation on the basis of Equation 9 gives the results shown in Table I.

These values of R are in excellent agreement with the value $R = 0.0250$ obtained by calibration with a mercury thread. The value 72.4 dynes per cm. for γ agrees well with the value of the surface tension of water at 20° C., 72.75 dynes per cm. (*4*). The value obtained with the advancing meniscus, 70.1 dynes per cm., is significantly lower than the other, but

agrees closely with a number of similar determinations made by the authors, and with the value (70.2 dynes per cm.) obtained by Washburn (*9*) with an advancing meniscus (though at a slightly higher temperature).

Table I. Water in Glass Capillary at 20° C.

Curve	Meniscus	Intercept	Slope	R	γ
		Dynes/cm.	*Dynes*	*Cm.*	*Dynes/cm.*
1	Advancing	−0.1011	3.786	0.0252	70.1
2	Receding	−0.1006	3.888	0.0251	72.4

L_1 = 2.5 cm.
α = 9°22′.

The experiment just cited is of interest here in supporting the theory discussed above. It has independent merit, however, in affording a simple method of determining surface tension under dynamic rather than under static conditions. The computation of results is simplified by using a horizontal capillary, so that $\alpha = 0$, in which case Equation 9 can be integrated to give

$$L^2 = \frac{R\gamma}{2\eta} t$$

Although in this case it is necessary to make a separate determination of the capillary radius, γ can be computed much more simply, as a direct plot of L^2 versus t gives a straight line of slope $R\gamma/2\eta$. In Figure 3 are plotted data for the penetration of water into a dry and into a wet horizontal glass capillary of radius 0.03556 cm. at 26° C. The value (70.3 dynes per cm.) obtained with the wet capillary agrees closely with the value (70.1 dynes per cm.) cited above for penetration into an inclined capillary at 20° C. and with Washburn's value of 70.2 dynes per cm. at 30° C. The extremely low value (38.5 dynes per cm.) found for penetration into a dry capillary has been checked by a number of careful repetitions of the experiment, and similar low values have been observed by others using different methods, notably Haller (*3*). No discussion of this phenomenon will be attempted here, but it is cited to illustrate the importance in penetration studies of determining interfacial forces under dynamic conditions comparable with those obtaining in the type of penetration under consideration.

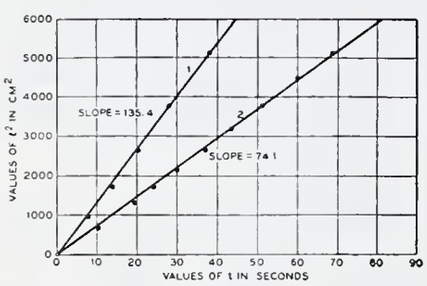

Figure 3. L^2 vs. t for Water in Horizontal Glass Capillary

1. Capillary wet
2. Capillary dry

Experimental: Paper Strips

In studying the rate of penetration into paper, strips of filter paper about 1.0 cm. wide and about 20 cm. long were employed. These were marked lightly with pencil at each half-centimeter along the length. In each test a strip was suspended vertically with its lower end dipping into the liquid. The liquid could be seen to rise in the strips, the upper borders of the wetted portion usually being even and horizontal and always clearly demarcated from the unwetted portion. The time at which the rising liquid reached each half-centimeter marking was read with a stop watch and recorded. Having thus determined corresponding values of height of rise, h, and time, t, values of the rate of rise, dh/dt, were obtained by graphical differentiation, and plotted against corresponding values of $1/h$.

To reduce evaporation as much as possible, the strip was suspended over the liquid in a closed system. The apparatus employed in the tests reported below is shown in Figure 4. The strip is fastened at both ends to hooks on a glass rod which is suspended by a fine wire from a glass windlass by means of which it can be raised or lowered. An ordinary stopcock above the windlass can be opened to evacuate the system if desired. The bulb sealed to the side of the main tube permits the atmosphere in the latter to be dried or brought to any desired humidity. With this arrangement, the vapor in the tube can be brought into equilibrium with the liquid, and the sample lowered into contact with the liquid without disturbing this equilibrium.

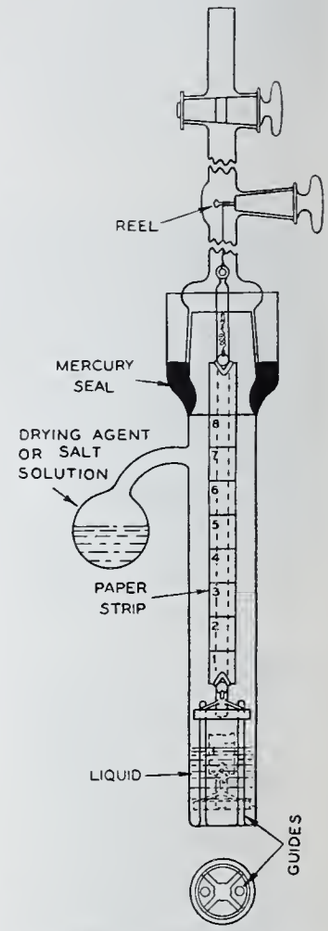

Figure 4. Apparatus for Studying Penetration of Liquids into Paper Strips

In Figure 5 are shown the results obtained on the penetration of liquids into a paper strip, as computed from data obtained as described above. The corresponding values of dh/dt and $1/h$ give a good fit to a straight-line relationship, in agreement with the theory developed above. This agreement was found with all liquids examined—namely, benzene, ethyl benzene, carbon tetrachloride, ethyl alcohol, methyl alcohol, and ethylene dichloride. In another article (*5*) the method is shown to apply to studies of the penetration of molten waxes into paper strips.

In Table II are listed the values of slope and intercept obtained in four runs made with each of the liquids tested. The approximate temperature of each run is noted in the table. For each value of slope and intercept there have been computed the corresponding values of $A\gamma$ (or 4η times the slope) and of B (or $8\eta/dg$ times the intercept) as given by Equation 7. For each liquid the mean values of $A\gamma$ and of B thus obtained are listed in Table III, together with the standard (or root mean square) deviations of the individual values from their mean, as a measure of the reproducibility of the results. The standard deviations of B are given in the same units as the values of B (sq. cm.), while the standard deviations of $A\gamma$ are expressed as percentages of the corresponding values of $A\gamma$.

In Table III are included the grand mean value of B and the mean values of the standard deviations of $A\gamma$ and of B. Taking each of these latter quantities as an estimate of the expected value of σ in samples of size four, the standard deviation (σ') of a single determination will be given by the relation $\sigma = 0.798\ \sigma'$ (*8*, p. 185). The value of σ' for $A\gamma$ is thus found to be 3.8 per cent (corresponding to a probable error of about 2.5 per cent for a single determination, or of about 1.3 per cent for the mean of four determinations). Variability of this magnitude may be ascribed wholly to the experimental error of the method.

As, for such fine capillaries, the hydrostatic head has but a small effect on the rate during the earlier stage of penetration, the intercept which measures this effect is so small that a

Table II. Values of Slope and Intercept

Liquid	Temp.	Slope	Intercept
	° C.	Sq. cm./sec.	Cm./sec.
Benzene	29.8	0.081	0.0030
	29.8	0.082	0.0024
	30.6	0.089	0.0032
	31.4	0.085	0.0025
Carbon tetrachloride	24.5	0.048	0.0022
	24.2	0.047	0.0026
	25.3	0.052	0.0028
	24.8	0.048	0.0024
Ethyl alcohol	26.5	0.036	0.0006
	25.9	0.035	0.0005
	24.7	0.032	0.0003
	25.0	0.033	0.0006
Ethyl benzene	30.9	0.080	0.0018
	32.2	0.086	0.0021
	31.7	0.072	0.0004
	27.9	0.076	0.0004
Ethylene dichloride	27.9	0.070	0.0024
	28.1	0.074	0.0022
	27.8	0.076	0.0023
	27.8	0.068	0.0019
Methyl alcohol	25.5	0.070	0.0020
	26.0	0.066	0.0017
	26.3	0.072	0.0020
	26.8	0.067	0.0009

Table III. Mean Values of $A\gamma$ and B

Liquid	$A\gamma$	σ	B	σ
	Dynes	%	Sq. cm.	Sq. cm.
Benzene	0.00188	3.3	13.05×10^{-8}	1.58×10^{-8}
Carbon tetrachloride	0.00177	3.3	11.70×10^{-8}	1.03×10^{-8}
Ethyl alcohol	0.00146	3.3	5.60×10^{-8}	1.35×10^{-8}
Ethyl benzene	0.00184	6.2	6.55×10^{-8}	4.35×10^{-8}
Ethylene dichloride	0.00212	3.0	10.80×10^{-8}	0.90×10^{-8}
Methyl alcohol	0.00149	3.8	9.30×10^{-8}	2.58×10^{-8}
Mean values		3.82	9.50×10^{-8}	1.97×10^{-8}

quite small experimental error will serve to explain the large percentage errors in B listed in Table III. The quantity B is of interest principally in affording a check on the theory given above, according to which it should depend only on the pore distribution in the paper strips, and be independent of the liquid tested. Hence the values of B obtained with the different liquids, as listed in Table III, should show no greater variation than the random one associated with variability of the order observed in individual determinations with a single liquid. This condition requires that each individual determination differ from the grand mean value (9.5×10^{-8} sq. cm.) by less than $3\ \sigma'$, where σ' is the standard deviation of individual determinations, which has the value 2.5×10^{-8} sq. cm., when computed as described above. Also this condition requires that the mean value for each liquid shall differ from the grand mean value by less than $3\sigma'/\sqrt{4}$ (*8*, p. 309). Except for the mean value of ethyl alcohol, which lies just outside the limits, all these conditions are satisfied. It seems reasonable to conclude that these data support the theory in showing B to be independent of the liquid tested.

A complete experimental check of Equation 7 is impossible, lacking a method for independently determining the distribution of pore sizes. A rough qualitative check, however, can be made by computing from the experimental data the range of pore sizes that would correspond to a uniform pore distribution. For this computation B can be taken as having the grand mean value of Table III (9.5×10^{-8} sq. cm.) and A as given by the mean value of $A\gamma$ for benzene, assuming (for reasons discussed below) that for this liquid γ is equal to its surface tension (27.6 dynes per cm.), so that $A = 68.1 \times 10^{-6}$ cm. From these values it follows that $A/\sqrt{B} = 0.221$, to which corresponds the value 0.10 for x in Figure 1. This permits A/R to be evaluated, giving $R = 0.004$ cm. and $xR = 0.0004$ cm. Hence, on the assumption of a uniform distribution, the range of pore sizes would be from 0.0004 to 0.004 cm.

That the actual pore sizes are of this order of magnitude can be seen from the photomicrographs shown in Figure 6 of thin cross sections of the paper used in these tests, which were prepared by Miss A. K. Marshall, of these laboratories.[1]

In Figure 6, A and B were taken from nearby points in a single section, and illustrate the considerable variation in density apparent in the paper. It is evident from these pictures that any attempt to represent the channels between fibers by a system of circular capillaries must be necessarily highly approximate. Comparison of the spaces between fibers with the scale shown in the figures, which has a total length (when reduced by the magnification factor) of 0.05 cm., shows that the mean diameter of the largest of these spaces is of the order of 0.005 cm. This is in fairly good agreement with the maximum mean diameter of 0.008 cm. calculated as described above.

Table IV. Relative Values for γ

Liquid	Average Temp.	γ (Relative)	S_{LG}	S_{LG} (Relative)
	° C.		Dynes/cm.	
Benzene	30	1.000	27.6	1.000
Carbon tetrachloride	25	0.942	26.1	0.946
Ethyl alcohol	26	0.779	21.8	0.790
Ethyl benzene	31	0.983	28.0	1.014
Ethylene dichloride	28	1.133	31.2	1.130
Methyl alcohol	26	0.794	22.1	0.800

Having thus subjected Equation 7 to such comparison with experimental results as is possible, it may be tentatively assumed to apply, and relative values of γ may be computed for the liquids tested from the values of $A\gamma$ listed in Table III. In Table IV are given such relative values for γ, taking that for benzene as 1.00. In the same table are listed for comparison values (at the average temperature of test) of S_{LG}, or the values of the surface tension of these liquids, as given in the International Critical Tables. In a third column are given values of S_{LG}, relative to benzene (1.00). The observed and computed values of relative surface tension agree well within the estimated precision of $A\gamma$. As it would be very unlikely that these liquids would all have the same contact angle unless the latter were zero, it was concluded that for all these liquids the contact angle against paper is either zero or very small.

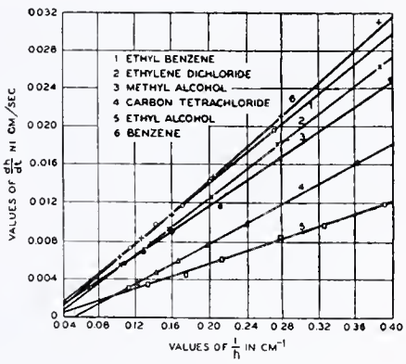

Figure 5. dh/dt vs. $1/h$ for Several Liquids in Filter Paper

Displacement Tests

By putting two immiscible liquids in a single vessel with a strip of paper projecting through the surface of separation, one liquid can be made to displace the other, and the rate of penetration of the displacing liquid can be observed and measured. The theory for this case can be worked out on lines analogous to the treatment given above of simple penetration, the effective force at the interface being the difference in adhesion tensions (γ') given by Equation 3. Experimentally it was found easy to observe and time such displace-

[1] A strip of paper was embedded in a block of paraffin and sectioned with a microtome in a plane normal to the length of the strip. The section was fastened to a slide, the paraffin dissolved out, the fibers stained with eosin, and photographs taken at a magnification of 122. It should be noted that the direction in which the microtome moved in making the cut was at right angles to the width of the strip, and it is therefore evident from the pictures that the fibers were cut clean and not dragged out.

ment in the cases of water and benzene, and water and carbon tetrachloride. Unfortunately, however, the results were not consistent or reproducible, presumably because of the unusual sensitivity of water surfaces to the presence of foreign materials. As there are few pairs of immiscible liquids of practical interest that do not include water as one of the liquids, the study of this displacement test was not pursued further. It is possible, however, that in porous media other than paper results would be obtained of sufficient constancy to make the displacement test a useful method of determining adhesion tension. The theory for such cases may be readily developed along the lines indicated.

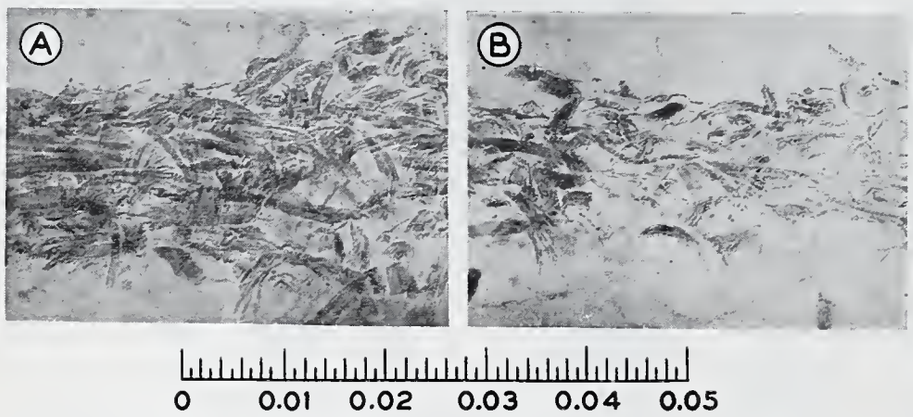

Figure 6. Photomicrographs of Paper Used in Tests

Summary

The theory presented above for capillary penetration into fibrous materials is an extension of that developed by Washburn for uniform capillaries. It has been shown that this simpler case may be conveniently studied in terms of the relation between rate of penetration and the reciprocal of the distance penetrated, and that in this way both the radius of the capillary and the penetration tension may be computed from the test data. The method is of value in that the measurement is made under dynamic conditions.

It has been shown that the treatment for penetration into a porous medium is similar to that for a uniform capillary, save that consideration must be given to the fact that the variation in pore size causes the resistance to viscous flow of each channel to be similar to that of a number of capillaries in series. The final expression therefore involves quantities whose values depend on the distribution of pore sizes. The general character of these quantities has been indicated by evaluating them for the case of a uniform distribution of pore sizes.

Data have been presented on the penetration of six organic fluids into strips of filter paper. It has been shown that these data agree with the theory in character. These experiments have been directed entirely to checking the validity of the theory presented. Such a check cannot be complete, and must be supported by the mutual consistency of results obtained in further work. Assuming the theory to be sufficiently accurate to justify its use in interpreting data, it permits the determination of relative values of penetration tension in paper and further studies may show it to be applicable to textiles and thin wood sections. The experimental procedure requires merely the measurement of the rate of rise of the liquid in a strip of the material, the strip and the liquid in which it dips being held in a vessel closed to prevent evaporation. By plotting the observed liquid height, h, against time, t, the rate of rise, dh/dt, may be evaluated graphically and plotted against $1/h$. This latter plot is a straight line of slope proportional to γ/η (the ratio of penetration tension to viscosity), the slope being a function of the distribution of pore sizes in the medium.

Values of the viscosity of the liquid multiplied by the slope of the plot of dh/dt versus h give, therefore, relative values of penetration tension for liquids tested with a given medium. Comparison of the values of penetration tension for a single liquid and several different media can be made only when it is known that the media are identical in pore structure or in the distribution of pore sizes, or when tests can be made with a reference liquid which is known to have a zero contact angle with all the media to be tested.

While the method of analysis given applies primarily to fibrous materials in which the rate of rise may be observed directly, it may be used to interpret data on the rate of penetration into porous systems for which only the rate of weight increase by penetration is known, provided the mean cross-sectional area of pore space is known, so that the linear rate of penetration can be calculated.

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Fire-Hazard Tests with Cigarets. Tests have been conducted in the fire-resistance section of the Bureau of Standards to determine the fire hazard of discarded lighted cigarets. The efficacy of certain modifications, such as slow-burning paper and the application of tips over one end, was also investigated. The burning cigarets were placed on representative specimens of grass and forest floor materials.

Under the conditions of the test, with the most favorable drafts and with relative humidities in the range 25 to 50 per cent, fires were caused on the average by 9 out of 10 lighted half-length untipped fast-burning cigarets discarded on grass, forest litter, or duff. The percentage of cases resulting in fires increased somewhat with decrease in relative humidity. The fire hazard of the slow-burning cigaret was much lower than for the fast-burning type. In the former the glow will not progress appreciably after the cigaret is discarded, while the latter will continue to glow until fully consumed.

The fire hazard of discarded lighted cigarets can be decreased by applying tips of cigaret paper. In tests with half-length fast-burning cigarets having tips 1 inch long of paper similar to that used on this type of cigaret, 4 fires occurred on the average for every 10 trials. With tips of the same length made of the paper used on slow-burning cigarets, the occurrence of fire in the exposed materials was reduced to 1 out of 4 trials.

Physical Evaluation of Finishes

A. E. Schuh and H. C. Theuerer, Bell Telephone Laboratories, Inc., New York, N. Y.

When tests measuring abrasion and impact resistance and distensibility are performed periodically on properly prepared finish panels which are aged under controlled environments, a new and highly useful tool is provided for the paint technologist.

Whereas in the customary method of exposure testing, the length of time required to produce visible failure must be taken as the chief index of quality of a finish, with this newer testing procedure the entire life of a finish can be followed. The weaknesses that presage failure may be detected. Reliable selection of improved materials is expedited because failure does not have to be awaited before such selection is made. It is also possible to obtain a clearer insight into the relative intensity of aging factors found in the environment.

In a previous paper (*1*), Schuh described a number of new physical tests suitable for the evaluation of the durability of organic finish coatings. Based on the concept that the aging of all these coatings is accompanied by similar types of measurable physical changes, it was pointed out that a program of testing might be devised which would allow the prognostication of the life of a finish in a manner that is less time-consuming and more reliable than the customary methods of exposure and simulated service tests. These ideas have now been applied for 3 years and their satisfactory use has led to several definite convictions.

The consumer of finishing materials is more interested in the health of a finish than in the manner of its death. In the customary methods of exposing finishes, the paint technologist is forced to act too much as the coroner and too little as the diagnostician. It has now been definitely learned that by the time visible signs of failure make their appearance, question as to whether the finish has finally failed by checking, cracking, or scaling becomes really a matter of quibbling. If the health and strength of a finish could be measured and followed in its youth and maturity, serious organic defects could be spotted and in the hands of the intelligent formulator immediately corrected.

Not only does exposure testing usually yield too little information for the effort expended, but it is permanently limited to a relative basis of comparison. This would not be such a serious drawback provided some "normal" exposure condition for purpose of reference could be found. Obviously environment plays as large a part in determining the durability of coatings as composition. On what basis then shall a normal exposure condition for purpose of reference be selected? The variables of temperature, humidity, sunshine, frequency of change, etc., are all beyond control and each affects a finish differently.

Considerable effort continues to be devoted to the development of synthetic weathering conditions in which the factors of environment are controlled and intensified to bring about acceleration of the degradation of finishes. After many years, it is now being realized that the search for a universal accelerated weathering cycle is futile. Even in cycles which appear to be reasonably satisfactory for certain types of finishes, comparisons in order to be safe cannot be made too general and must be limited to gross differences. The chief value of this accelerated exposure work appears to lie in the fact that considerable light has been shed on the relation between intensity of environmental factors and the life period of finishes. Benefiting by this information the authors have sought to follow the effect of these aging factors quantitatively during the complete life of the finish.

In this paper, for the purpose of illustrating what can be learned regarding the durability of finishes by analysis of their physical behavior during the period of their serviceable condition, the authors report a study carried on for the past 2 years on automotive vehicle finishes. This study included a wide variety of finishing materials in the nitrocellulose lacquer, older type of oleoresinous, and modern synthetic fields. Not only were the individual components, such as primers, surfacers, and color enamels, examined by themselves with regard to their physical behavior, but the effect of combining these materials into the recommended finish systems was studied.

The physical aging of such systems was followed under two sets of controlled environmental conditions, one set being mild and extending over a period of 14 months and the other drastic and lasting only 3 months. Correlative data on outdoor panel exposures both in Florida and New York and on actual service tests on trucks in both Florida and northern areas have been furnished.[1] In addition, the effect of building up systems with and without thick surfacing materials has been investigated.

In the course of this study various shortcomings of the tests were revealed, and the need for certain future studies that will be of interest to the paint technologist was clearly evidenced.

Description of Tests

In a general qualitative manner, a good finish is one which satisfies appearance requirements, is tough, and adheres well to its base. Not only should these requirements be met initially, but ideally, no change should occur with age. It is the qualitative and yet very apt term "toughness" which is most in need of quantitative clarification. Hardness, flexibility, impact, and abrasion resistance are all attributes of toughness, all relating to the deformability of finish coatings under different stresses. There is still considerable groping in trying to unravel the interrelations of the various rheologic properties measured in these tests. However, certain broad relations are becoming apparent. In the meantime the tests used in this study do provide quantitative measurements which are significant and reproducible, and in the future fewer and less ambiguous tests may be found adequate.

A brief description of the tests used in this study should aid in the discussion of the results recorded in the various tables. The wear test is exactly as reported in previous papers (*1*, *2*) and consists essentially of determining the number of grams of 180-mesh Carborundum required to abrade through unit thickness of coating. Since the materials were applied by means of a spray gun, uniformity of thick-

[1] For the data on outdoor exposures in Florida and New York and the data on actual service life of truck finishes, the authors gratefully acknowledge their indebtedness to F. F. Farnsworth and L. H. Campbell of this laboratory.

ness was not as good as might be desired. Hence, in addition to wear coefficients—that is, the number of grams of Carborundum required to wear through 2.54×10^{-3} cm. (0.001 inch) of coating—the actual thickness of the priming and top coats is given, as determined by means of a calibrated microscope at 600 diameters. A short clean scratch was made through the coatings by means of a razor blade held at 45°. The microscope was focused first on the top plane of the cut, then at the boundary between primer and enamel coats, and finally at the interface between primer and base metal surface. The sharp color difference between enamels, primers, and metal surface made the location of these interfaces a simple problem.

The test device for determining impact resistance has been modified. It was felt that the determination of the force level at which a finish shatters is of more significance than a knowledge of the number of repeated blows which a finish can withstand at any arbitrary force level. Consequently the impacting device was changed so that the hammer speed progressively increases and the r. p. m. at which shattering of the finish to the base metal first occurs is observed. If desired, the test can also be used as heretofore, for the determination of repeated impacts at any fixed speed of rotation.

This new modification has materially improved the precision of the test. Triplicate readings in 38 different determinations of repeated impact resistance performed at fixed speed gave an average deviation of 21 per cent. The average deviation in the case of the modified test, where limiting force of impact is determined, was 5 per cent. In the older form of test, the maximum deviation from the mean was as high as 57 per cent, whereas in the newer form 10.6 per cent was the maximum.

In the tables the type of failure produced on impact is also recorded. Some finishes fail by a gradual crumbling or wearing away, whereas others shatter over a considerable distance around the point of impact; hence an arbitrary rating of 1 to 3 in type of end point has been used, supplementary to the r. p. m. values of impact.

The mandrel test was used as previously described. Six different mandrel sizes—namely, of 0.125, 0.25, 0.375, 0.5, 0.75, and 1 inch (0.32, 0.63, 0.95, 1.27, 1.89, and 2.54 cm.) radius—were used. The mandrel size at which first cracking became noticeable under low-power magnification is reported as the limiting distensibility in terms of per cent elongation of the finish coating. The per cent elongation is calculated on the assumption that the neutral plane of movement in the panel—that is, the plane where distension and compression are equal—is in the exact center of the panel. However, on exceeding the limit of elasticity of the base material, this neutral plane unquestionably shifts, so that the calculated distension at the metal surface beneath the coating becomes only an approximation. Since the same base material was used throughout, the error is constant and the values are comparable. In addition to the value of distensibility, the character of the adhesion to the base metal after stretching is qualitatively noted. Four degrees of adhesion are arbitrarily recorded, varying between the extremes where the coating has been cleanly severed from the base to where a scuffing with a blunt tool leaves the finish intact.

In addition to the above three tests, the Pfund hardness was determined after 3 and 14 months of aging in the humidity cycle and after 32 weeks of aging in the weatherometer cycle, in order to obtain additional correlative information on the deformability changes of these coatings.

Examination of Primers, Surfacers, and Enamels

Of the several hundred different finishing materials investigated, a representative number are included in Tables I, II, and III, which show the extent of variation existing in the products obtainable in the market approximately 2 years ago. For purposes of comparison, values of abrasion resistance and distensibility are recorded. In addition, drying-time data are given in order to serve as a basis of differentiation between the older types of oleoresinous enamels and the more modern synthetic types. The exact composition of the materials tested is unknown; the consumer's interest is centered in the behavior of finishing materials and not their composition.

Table I. Primers[a]

Material	Wear[b]	Mandrel Elongation	Mandrel Adhesion	Drying Time Dust-free	Drying Time Through-dry
		%		*Min.*	*Min.*
A. Nitrocellulose					
P—101[c]	75	>17.7	Good	2	5
P—102	44	>17.7	Good	5	60
P—103	65	10.5	Good	4	10
P—104	24	>17.7	Fair	3	10
P—105	69	3.9	Good	5	10
P—106	61	3.9	Fair	5	15
P—107	9	5.7	None	3	6
P—108	64	<3	Fair	3	15
P—109[c]	42	<3	None	2	5
P—110	27	<3	None	3	9
P—111	26	<3	None	5	20
P—112	13	<3	None	1	5
				Hours	*Hours*
B. Oil Type					
P—201	337	>17.7	Good (soft film)	4	>24
P—202	190	>17.7	Good (soft film)	3.5	<24
P—203	66	>17.7	Good	2.5	>24
P—204	65	>17.7	Good	0.5	<24
P—205	60	>17.7	Good	0.5	<24
P—206[c]	60	>17.7	Good	2.5	5
P—207	59	>17.7	Good	2	5
P—208	51	>17.7	Good	>8	<24
P—209	45	>17.7	Good	4	<24
P—210	38	>17.7	Good	>7	<24
P—211[c]	24	>17.7	Good	0.16	2.75
P—212	24	>17.7	Fair	0.5	<24
P—213	55	17.7	Good	>7	<24
P—214	42	17.7	Good	0.5	1.25
P—215	42	17.7	Good	0.25	3
P—216[c]	41	17.7	Good	0.33	2
P—217	35	17.7	Good	0.5	3.5
P—218[c]	33	17.7	Good	3	5
P—219	47	10.5	Good	0.25	1.5
P—220	43	10.5	Good	1	5.25
P—221	42	10.5	Poor	0.33	4.25
P—222	10	10.5	Poor	0.25	2
P—223	8	10.5	Poor	0.16	2.75
P—224	45	5.7	Good	0.33	2
					2
C. Synthetic					
P—301	107	>17.7	Good	0.33	(Remains tacky)
P—302	47	>17.7	Good	0.2	0.5 (Gelled)
P—303	20	>17.7	Good	..	..
P—304	39	10.5	Fair	0.16	0.5
P—305	24	7.4	Good	0.16	0.5

[a] All materials listed in Tables I, II, and III air-dried 1 week and exposed to 140° F. (60° C.) for 3 weeks prior to test.
[b] Wear values in Table I and succeeding tables are expressed in terms of grams of Carborundum per 2.54×10^{-3} cm. (0.001 inch) of coating.
[c] Materials used in subsequent tables.

Code used for identification of materials in all tables:

P, primers	100 Series, nitrocellulose materials
E, enamels	200 Series, oil or oleoresinous materials
S, surfacers	300 Series, synthetic-type materials
G, putties	

Table II. Surfaces and Putties[a]

	Wear	Mandrel Elongation
		%
Nitrocellulose		
S—101	36	<3
S—102[b]	30	<3
G—101[b]	33	<3
Oil type		
S—201[b]	28	<3
G—201[b]	29	<3
Synthetic		
S—301[b]	23	<3
G—301[b]	26	5.7

[a] Materials air-dried 1 week and exposed to 140° F. (60° C.) for 3 weeks prior to test.
[b] Materials used in subsequent tables.

As can be seen from Table I, the nitrocellulose primers, with but a few exceptions, show poor distensibility. The oil-base primers are as a class highly distensible; as may be expected, quick drying is obtained at the expense of flexibility. On the other hand, the synthetic-type primers combine quick drying with distensibility. The surfacers and putties (Table II), whether of nitrocellulose or oleoresinous character, lack cohesional strength, as shown by the low wear and mandrel-test values. The color enamels (Table III) show a spread of values similar to that of the primers. It is surprising how relatively brittle the majority of nitrocellulose enamels are. In the synthetic field, the dust-free stage of drying is reached as a rule within 1 hour, thus permitting quick recoating; in some cases, however, the through-dry stage is very much delayed, the materials exhibiting a slight tack 24 hours after application.

Table III. Color Coats[a]

	Mandrel Wear	Mandrel Elongation	Mandrel Adhesion	Drying Time Dust-free	Drying Time Through-dry
		%		*Min.*	*Min.*
Nitrocellulose					
E—101[b]	130	>17.7	Good	3	5
E—102[b]	92	>17.7	Good	5	20
E—103[b]	79	>17.7	Good	5	12
E—104	82	>17.7	Good	5	12
E—105	61	10.5	Poor	4	15
E—106[b]	39	10.5	Poor	8	30
E—107	94	<3	None	4	11
E—108	73	<3	None	5	10
E—109	69	<3	None	6	10
E—110	65	<3	None	5	12
E—111	64	<3	None	3	5
E—112	61	<3	None	2	5
E—113	61	<3	None	3	7
E—114	61	<3	None	2	5
E—115	57	<3	None	4	8
E—116[b]	48	<3	None	6	20
E—117	46	<3	None	3	10
E—118[b]	43	<3	None	4	10
E—119	40	<3	None	3	8
E—120	39	<3	None	8	15
E—121	36	<3	None	3	10
E—122	37	<3	None	4	8
				Hours	*Hours*
Oil type					
E—201	130	>17.7	Good	4.25	<24
E—202	91	>17.7	Good	3.75	<24
E—203	87	>17.7	Good	4.25	<24
E—204	86	>17.7	Good	7	<24
E—205	83	>17.7	Good	3	8
E—206[b]	82	>17.7	Good	3.5	<24
E—207[b]	72	>17.7	Good	3.75	<24
E—208	69	>17.7	Good	4	8
E—209	115	17.7	Good	3.5	<24
E—210	93	17.7	Good	2	4.5
E—211	76	17.7	Good	3.5	6.5
E—212	70	17.7	Good	3	<24
E—213[b]	53	17.7	Good	0.33	<24
E—214	69	10.5	Good	2.75	5.25
E—215	60	10.5	Good	1.5	6.25
E—216	34	7.4	Poor	0.33	3.25
E—217	61	3.9	Poor	1	2.5
Synthetic					
E—301	117	>17.7	Good	1.25	2
E—302	102	>17.7	Good	3.25	<24
E—304[b]	100	>17.7	Good	0.5	24 (Slight tack)
E—305	96	>17.7	Good	0.33	24 (Slight tack)
E—306	93	>17.7	Good	....	... (Gelled)
E—307	79	>17.7	Good	0.16	<24 (Slight tack)
E—308	98	17.7	Good	0.25	<24 (Slight tack)
E—309	120	10.5	Good	1	2

[a] Materials air-dried 1 week and exposed to 140° F. (60° C.) for 3 weeks prior to test.
[b] Materials used in subsequent tables.

Although it was not expected that a knowledge of the deformability of the individual components would reveal much regarding the performance of automotive finish systems built up from these components, actually these finishing systems, particularly when exposed on wood panels in Miami, Fla., failed almost quantitatively in the order and manner one might predict from the data in Tables I, II, and III. Thus a system in which both primer and color enamel were flexible lasted over four times as long as a system in which both these components were brittle. Not only was this latter system short-lived, but on failing the wood was laid bare over large areas. Furthermore, a system in which the top coat was brittle and the priming coat flexible, on failing, merely exposed the intact primer. Table IV illustrates the point.

Table IV. Automotive Finish Systems

Type of System	Materials Used	Elongation	Florida Exposure Results[a]
		%	
Brittle primer Brittle enamel	P—109 E—118	<3 <3	In 3 months entire system had chipped away from wood
Brittle primer Brittle enamel	P—108 E—113	<3 <3	In 3 months entire system had chipped away from wood
Flexible primer Flexible enamel	P—211 E—103	>17.7 >17.7	No cracking, checking, or scaling in 12 months
Flexible primer Flexible enamel	P—218 E—102	17.7 >17.7	No cracking, checking, or scaling in 12 months
Flexible primer Brittle enamel	P—208 E—121	>17.7 <3	In 4.5 months enamel scaled badly; primer intact

[a] Oak panels exposed outdoors 45° facing south.

Finish Systems and Aging

The appropriate primers, surfacers, and color enamels were combined according to the recommendations of the suppliers and the sample panels exposed to two different exposure cycles.

Clean but otherwise unprepared mild steel panels were used and the materials applied by spray. It was attempted to apply the priming coats to a thickness of 1.27×10^{-3} cm. (0.0005 inch) and the two color coats to a thickness of approximately twice that value. The surfacing coats were applied and rubbed down to the primer surface before applying the top coats. All panels were allowed to age 3 months at 75° F. (23.89° C.) and 50 per cent relative humidity prior to exposure to the special cycles and the first set (set I of Tables V and VI) was subjected to test at this point. Three additional sets of panels were then exposed to a cycle consisting of 3 days at 95° F. (35° C.) and 90 per cent relative humidity, 1 day at 125° F. (51.67° C.) and 15 per cent relative humidity, and 3 days at 75° F. (23.89° C.) and 50 per cent relative humidity, after which the cycle was repeated. At the end of 2 months of exposure set II was tested. At the end of 8 and 14 months the third and fourth sets of panels were tested. In every case the tests were performed at 75° F. (23.89° C.) and 50 per cent relative humidity, 24 hours being allowed for the materials to reach equilibrium. Without thickness control of the coatings, control of the temperature and humidity at time of test, and control of exposure environment between tests, periodic testing of duplicate panels would lose significance. The results of this series of tests are recorded in Table V.

In a second series, the panels were exposed to a weatherometer cycle, similar to the Atlas Weather-Ometer, familiar to the paint technologist. In the machine used in this study the panels are mounted on a drum which rotates twice an hour. At one side a gentle water spray impinges against the panels. Illumination and heating of the panels is effected by means of a carbon arc lamp. The temperature range at the panel surface lies between 140° and 70° F. (60° and 21.11° C.) One hour a week the panels are chilled to approximately −10° F. (−23.33° C.) and immediately heated for 1 hour at 140° F. (60° C.), after which they are inspected. Thus in 1 week the panels are subjected to over 300 thermal shocks and to the possibility of photochemical reactivity at wave lengths down to 2756 Å. The stress induced by the action of surface wetting and drying is probably not severe, owing to the frequency of change and the time lag in absorption and desorption of water in the coatings.

Set V was tested at the end of 6 weeks' exposure to this cycle and set VI at the end of 12 weeks. A record was kept of appearance changes at the end of every 2 weeks. The physical test results of this series are recorded in Table VI, and the visual data on exposure and outdoor exposure both in Miami, Fla., and New York City are recorded in Table VII.

Although a large number of finish systems was tested, only a sufficient number was selected for presentation in Tables V, VI, and VII to illustrate the type of information that can be obtained from physical tests. Four types of systems are illustrated, one in which a nitrocellulose primer is followed by two coats of lacquer enamels and the other three where oil-base primers are coated with two coats of lacquer enamels,

Table V. Humidity Cycle

	Material	Wear Set I T[a]	Wear Set I W[b]	Wear Set II T[a]	Wear Set II W[b]	Wear Set III T[a]	Wear Set III W[b]	Wear Set IV T[a]	Wear Set IV W[b]	Impact Set I R. p. m.	Impact Set I End point[c]	Impact Set II R. p. m.	Impact Set II End point[c]	Impact Set III R. p. m.	Impact Set III End point[c]	Impact Set IV R. p. m.	Impact Set IV End point[c]	Mandrel Set I Elong. %	Mandrel Set I Adh.	Mandrel Set II Elong. %	Mandrel Set II Adh.	Mandrel Set III Elong. %	Mandrel Set III Adh.	Mandrel Set IV Elong. %	Mandrel Set IV Adh.	Pfund Hardness[d] Set I	Pfund Hardness[d] Set IV
	N-C primer + N-C enamel																										
A.	P—101	1.02	42	1.27	62	1.52	56	0.76	75	>1500	1	>1500	1	>1500	1	>1500	1	>17.7	Good	>17.7	Good	>17.7	Good	>17.7	Good	255	230
	E—101	2.03	93	1.52	100	1.78	110	1.52	93	>1500		>1500		1035		765											
B.	P—109	1.27	35	1.27	26	1.78	39	1.52	21	650	2	650	2	520	2	465	2	<3	None	<3	None	<3	None	<3	None	1050	815
	E—118	2.29	41	1.78	45	1.78	52	2.03	37																		
	Oil primer + N-C enamel																										
C.	P—218	2.03	19	1.27	36	1.27	36	1.78	32	700	2	500	2	535	2	400	2	>17.7	Fair	>17.7	Fair	>17.7	Fair	10.5	Poor	60	255
	E—102	3.30	66	2.29	70	3.05	70	2.79	75																		
D.	P—211	1.27	32	0.76	38	0.76	41	0.76	38	430	1	900	1	555	1	400	1	>17.7	Good	>17.7	Good	>17.7	Good	3.9	Fair	270	280
	E—103	2.03	58	1.27	75	1.52	74	1.78	53																		
E.	P—216	1.02	41	0.76	36	1.02	44	1.02	38	670	1	960	2	670	2	725	2	<3	Fair	<3	Fair	<3	None	<3	None	1045	840
	E—116	2.03	40	1.52	41	2.03	45	1.52	46																		
F.	P—206	0.76	27	0.76	38	0.76	34	0.76	31	780	2	740	2	620	2	500	2	17.7	Fair	10.5	Fair	<3	Poor	<3	Poor	260	765
	E—106	2.29	52	2.29	44	2.54	50	2.03	43																		
	Oil primer + enamel																										
G.	P—216	0.76	23	0.76	38	0.76	49	0.51	46	760	1	950	1	940	2	765	2	>17.7	Fair	>17.7	Fair	17.7	Fair	<3	None	50	315
	E—207	2.54	59	3.30	47	2.54	52	2.79	49																		
H.	P—206	2.03	27	1.52	43	1.52	26	1.52	32	670	2	600	2	600	2	520	2	>17.7	Fair	>17.7	Fair	17.7	Fair	<3	Fair	60	510
	E—206	2.54	46	3.05	46	2.29	64	2.29	56																		
	Oil primer + synthetic enamel Type color coats																										
I.	P—216	0.76	25	1.27	28	0.51	54	0.76	53	700	1	780	1	985	1	800	1	>17.7	Good	>17.7	Good	17.7	Good	7.4	Good	425	410
	E—310	2.03	58	1.52	64	1.52	65	1.78	63																		
J.	P—218	1.52	28	1.02	27	1.02	38	0.76	45	550	1	550	1	535	1	465	2	>17.7	Fair	>17.7	Good	7.4	Fair	<3	None	345	515
	E—304	2.03	73	1.78	76	2.03	76	1.52	76																		

All panels aged 3 months at 75° F. and 50 per cent relative humidity before exposure to humidity cycle.
Series I, tested at this initial point.
Series II, tested after 2 months' exposure to humidity cycle.
Series III, tested after 8 months' exposure to humidity cycle.
Series IV, tested after 14 months' exposure to humidity cycle.

[a] Thickness, in 10^3 cm.
[b] Grams of Carborundum required to abrade through 2.54×10^{-3} cm. (0.001 inch) of coating.
[c] 1, Crumbling away at point of impact, no shattering; 2, medium shattering around point of impact; 3, serious shattering around point of impact.
[d] Grams at 3 div.

Table VI. Weatherometer Cycle

	Material	Wear Set I T[a]	Wear Set I W[b]	Wear Set V T[a]	Wear Set V W[b]	Wear Set VI T[a]	Wear Set VI W[b]	Impact Set I R. p. m.	Impact Set I End point[c]	Impact Set V R. p. m.	Impact Set V End point[c]	Impact Set VI R. p. m.	Impact Set VI End point[c]	Mandrel Set I Elong. %	Mandrel Set I Adh.	Mandrel Set V Elong. %	Mandrel Set V Adh.	Mandrel Set VI Elong. %	Mandrel Set VI Adh.	Pfund Hardness[d] Set I	Pfund Hardness[d] Set VI
	N-C primer + N-C enamel																				
A.	P—101	1.02	42	1.27	74	1.27	74	>1500	1	>1500	1	900	1	>17.7	Good	<3	Fair	<3	Poor	255	785
	E—101	2.03	93	1.52	101	1.52	80	>1500		1500		700									
B.	P—109	1.27	35	1.78	26	1.27	18	650	2	520	2	400	2	<3	None	<3	None	<3	None	1050	1050
	E—118	2.29	41	1.78	30	1.27	24														
	Oil primer + N-C enamel																				
C.	P—218	2.03	19	1.52	33	1.78	35	700	2	620	2	400	2	>17.7	Fair	<3	Poor	<3	Poor	60	310
	E—102	3.30	66	2.29	86	3.05	70														
D.	P—211	1.27	32	0.76	35	0.76	47	430	1	567	2	400	2	>17.7	Good	<3	Fair	<3	Fair	270	625
	E—103	2.03	58	1.78	64	1.27	64														
E.	P—216	1.02	41	1.02	40	0.51	54	670	1	800	1	400	1	<3	Fair	<3	Fair	<3	None	1045	915
	E—116	2.03	40	1.52	35	1.52	29														
F.	P—206	0.76	27	1.02	27	0.76	13	780	2	500	1	400	1	17.7	Fair	<3	Poor	<3	Poor	260	45
	E—106	2.29	52	2.29	33	2.29	24														
	Oil primer + enamel																				
G.	P—216	0.76	23	0.76	40	0.51	47	760	1	1035	1	545	1	>17.7	Fair	5.7	Fair	<3	None	50	745
	E—207	2.54	59	2.29	65	2.03	57														
H.	P—206	2.03	27	2.29	36	0.76	40	670	2	700	2	500	2	>17.7	Fair	<3	Fair	<3	Fair	60	640
	E—206	2.54	46	1.78	69	2.03	64														
	Oil primer + synthetic enamel																				
I.	P—216	0.76	25	0.76	37	0.76	43	700	1	980	1	455	1	>17.7	Good	<3	None	<3	None	425	750
	E—310	2.03	58	1.78	74	2.03	60														
J.	P—218	1.52	28	1.27	39	0.76	27	550	1	640	1	400	1	>17.7	Fair	3.9	Fair	<3	None	345	750
	E—304	2.03	73	1.52	76	1.52	91														

All panels aged 3 months at 75° F. and 50 per cent relative humidity before exposure to weatherometer cycle.
Set I, tested at this initial point.
Set V, tested after 6 weeks' exposure to the weatherometer cycle.
Set VI, tested after 12 weeks' exposure to the weatherometer cycle.

[a] Thickness, in 10^3 cm.
[b] Grams of Carborundum required to abrade through 2.54×10^{-3} cm. (0.001 inch) of coating.
[c] 1, Crumbling away at point of impact, no shattering; 2, medium shattering around point of impact; 3, serious shattering around point of impact.
[d] Grams at 3 div.

oleoresinous enamels, and synthetic enamels, respectively. In all cases the recommended surfacing coats were applied and sanded off as completely as possible without removing part of the priming coat.

After several years' experience in testing practically every conceivable type of finishing material, no case has yet been found where a finish improved with age, discounting a possible initial rise in the very early age of a film, or a condition in which a relatively new coating was subjected to a definitely higher temperature, thus allowing secondary flow to occur. An appreciation of this simple fact is important, inasmuch as an opportunity for safe selection is thus allowed in the early age of a film whenever the differences in quality between various materials are wide.

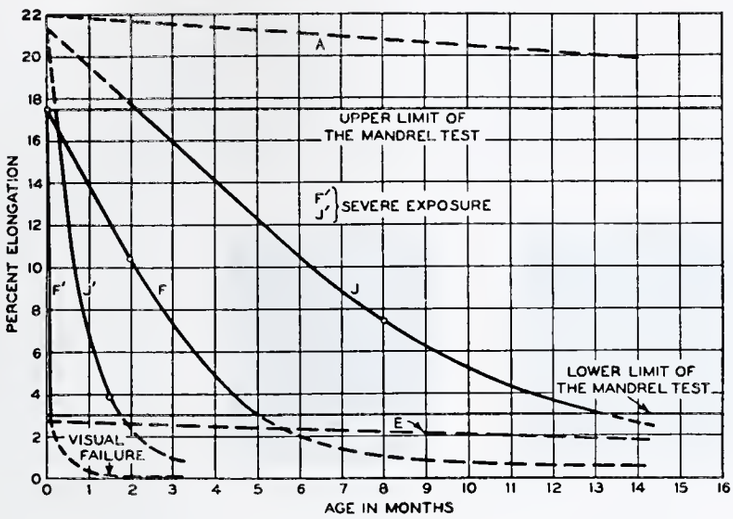

Figure 1. Loss of Distensibility of Finishes with Age

However, since the durability of finishes is more important than their initial quality, a series of periodic tests applied during the course of aging must show clearly the trends of change in the properties tested. It is on this basis that Tables V and VI must be examined and the validity of the selection of better materials confirmed by correlation with the information obtained on the exposure and service data in Tables VII and VIII.

When aging is taken into consideration the differentiation between materials becomes wide. Thus comparing the all-lacquer systems A and B, it is seen that system A, even at the end of 14 months' exposure, shows values in wear resistance, impact resistance, and distensibility very much higher than the initial values of system B. Comparing the oil-primer lacquer-enamel systems, the superiority of C and D over E and F becomes apparent. Exposure data definitely confirm these differences in quality.

However, several cases are shown in the tables in which the correlations between physical analysis and exposure tests are not so well defined. Thus, although examination of systems E and F in Tables V and VI shows that F has a very rapid rate of decline in per cent elongation, one would hardly anticipate the amount of difference between the two shown in the exposure data. Similarly in the case of systems G and H, although one would select G in preference to H, owing to its slower rate of decline and superior impact resistance, the wide difference in durability revealed on exposure would not be anticipated.

This has led to an appreciation of a critical weakness in the mandrel test—for the purpose of correlating film failure such as checking and cracking, the measurement of distensibilities considerably less than 3 per cent becomes of major importance, particularly when the coatings are applied over a metal base. The reason for this is probably as follows:

> One of the chief stresses that a coating on exposure must be able to cope with is the distension of the base material. It so happens that the coefficient of expansion of steel with temperature is low, a rise in temperature of 120° F. (48.89° C.) bringing about an expansion of approximately only 0.1 per cent. Although checking, cracking, and scaling may not be necessarily determined by the ability of the coating to move along with an expanding and contracting base, it is true that, when this compensating motion can no longer occur, failure must take place. It is also an experimental fact that in no case has checking occurred when the distensibilities were greater than 3 per cent. The point is further supported by the fact that when the same materials are coated on wood, distensibilities of a much higher order of magnitude become significant, since in this case, owing to the absorption and desorption of water, the surface of the base undergoes movements of the order of several per cent. This explains why failure of coatings on wood panels agreed so well with what might have been predicted from the distensibility data of the components that made up the finish systems.

If, then, the mandrel test were so modified as to permit the critical measurement of elongations lower than 3 per cent, it

Table VII. Exposure Data

	Material	Weatherometer[a] Initial gloss change	Weatherometer[a] Chalking	Weatherometer[a] Checking	Weatherometer[a] Cracking	Florida[b] Gloss after rubbing	Florida[b] Chalking	Florida[b] Checking	Florida[b] Cracking	New York[b] Gloss after rubbing	New York[b] Chalking	New York[b] Checking	New York[b] Cracking
		Weeks	*Weeks*	*Weeks*		*Months*	*Months*	*Months*	*Months*	*Months*	*Months*	*Months*	*Months*
	N-C primer + N-C enamel												
A.	P—101	12	12	None	None	.....	...	.....	....	....	...	....	....
	E—101												
B.	P—109	6	6	12	None	3, eggshell	3, def.	3, def.	3, none	3, fair	3, def.	3, slight	None
	E—118					10, flat							
	Oil primer + Px enamel												
C.	P—218	4	7	None	None	12, fair	3, def.	12, none	12, none	6, fair	6, def.	6, none	6, none
	E—102												
D.	P—211	12	10	None	None	12, fair	12, def.	12, none	12, none	7, fair	7, def.	7, none	7, none
	E—103												
E.	P—216	9	7	12	None	3, eggshell	3, def.	3, none	3, none	3, eggshell	3, def.	3, none	3, none
	E—116					6, eggshell	6 def.	6, def.	6, none	6, eggshell	6, def.	6, def.	6, none
						12, flat	12, def.	12, def.	12, def.				
F.	P—206	3	4	4, init.	None	3, fair	3, def.	3, def.	3, none	4, fair	4, def.	4, def.	4, none
	E—106			6, def.		5, fair	6, def.	6, def.	6, none				
				12, bad									
	Oil primer + enamels												
G.	P—216	4	2, init.	None	None	3, fair	3, def.	3, none	3, none	.....	...	....	....
	E—207		12, def.			6, fair	6, def.	6, none	6, none				
						12, eggshell	12, def.	12, none	12, none				
H.	P—206	4	4, init.	4, init.	None	3, eggshell	3, def.	3, slight	3, none	3, eggshell	6, def.	6, slight	6, none
	E—206		8, def.	8, def.									
	Oil primer + synthetic enamel												
I.	P—216	7	7	None	None	.....	...	.....	....	3, fair	3, def.	3, none	3, none
	E—310									6, fair	6, def.	6, none	6, none
J.	P—218	10	8	None	None	.....	...	.....	....	3, fair	3, def.	3, none	3, none
	E—304									6, fair	6, def.	6, none	6, none

[a] Panels inspected every 2 weeks.
[b] Panels inspected every 3 months.

is felt that a satisfactory elucidation would be provided for the hazy correlation between physical analysis and exposure in the systems E, F, G, and H. It is likely, that in the case of finishes exposed on metal panels, distensibilities of less than 1 per cent will be found to become critical. A method which it is hoped will permit the precise determination of per cent elongation of finish panels over a wider range of distensibility is now being investigated. With such a tool, the important problem of the relation between distensibility and adhesion to the base can be studied.

Figure 2. Effect of Surfacing Materials on Impact Resistance

1. P—211
E—103

2. P—211
S—102
E—103

3. P—211
S—102
G—101
S—102
E—103

Comparison of Tables V, VI, and VII shows clearly that a finish has fallen off seriously in its ability to conform to various stresses a long time prior to the point where visible failings begin to make their appearance. Thus, in the series exposed to a mild exposure cycle, even after 14 months no visible changes had occurred, even though most of the materials had suffered badly in deformability. Even more striking is the case of the panels exposed to the weatherometer cycle. All but two of the systems in Table VI showed elongations of less than 3 per cent after 6 weeks; after another 6 weeks all had fallen below the lower limit of the mandrel test. It appeared therefore that 12 weeks in the weatherometer had spelled the death of most of these finishes and yet six out of ten had not shown first signs of surface checking by the end of the exposure period. Two began to show this only at the end of 12 weeks' exposure. In the remaining two systems initial checking showed up at the end of 4 weeks. Quite likely the distensibility had dropped considerably below 3 per cent and hence was impossible of measurement by the mandrel test.

Comparisons of Tables V and VI also indicate that the relative intensity of aging factors in the two cycles employed is of the order 10 to 1, since these systems show comparable physical qualities at the end of 60 weeks of exposure in the mild cycle as compared to 6 weeks in the weatherometer. This is not so surprising when one considers that the total number of thermal shocks of approximately equal intensity to which these coatings were subjected is 100 times greater in the weatherometer cycle than is the slower humidity cycle. Possibly if these finishes were exposed on wood panels, the ratio of acceleration between the two cycles might not be so high, since in this case the coating would have to undergo much greater expansion in the slow cycle than in the rapidly fluctuating weatherometer cycle.

In Figure 1 the aging of several typical finish systems, as shown by changes in distensibility, is graphically represented. The wide differences inherent in these materials while they are still in serviceable condition are clearly shown. The curves are necessarily only approximate owing to the limitations of the mandrel test. The relative effect on the speed of degradation of cycles of different intensity is clearly exhibited.

Examination of Table VII shows that the order of failure under the three exposure conditions is approximately the same. The outdoor panels were mounted 45° facing south. All three exposures lead to the same order of selection as that obtained from the analysis of the physical data prior to visual failure. It appears that panels in the weatherometer fail in approximately one-third the time required to fail in Florida. The amount of chalking of the panels exposed in Florida was greater than at the other exposures. It is of interest to note that even on the matter of chalking, the materials which show up best under the physical tests also show the least chalking and gloss change.

By way of correlation to final service tests, 27 trucks (17 in the North and 10 in Florida) of which 15 were of all-metal construction and the rest wood and metal, were finished with various systems reported in Tables V and VI, and their serviceability in the field carefully followed. The results are shown in Table VIII. The length of service life for the various systems falls in the order one would expect from the data obtained both by the periodic physical tests and panel exposures. The determination of end of serviceability is of course open to some question, since standards of appearance necessarily involve elements of personal judgment.

Surfacer Study

The value of the physical tests discussed above is not limited to their use in foretelling the durability of finishes. Such problems as the effect on the mechanical behavior of a system caused by changes in the components that make up such a system can be clearly recognized. Thus in the finishing of automotive vehicles it is common practice to apply generous coats of surfacing materials in order to hide imperfection of the base metal. Recommended practice is to sand off excess surfacing materials. In order to learn what effect the presence of varying amounts of brittle surfacing material would have on a finish system made up of flexible primer and flexible enamels, an oil-primer nitrocellulose-enamel system, a complete oleoresinous system, and a complete synthetic type were selected for test. The thicknesses of the various components comprising the systems, values of abrasion resistance, impact resistance, and distensibility are given in Table IX.

Figure 3

The effect of brittle intermediate coats is marked. Thus, the impact resistance goes up definitely for the young film, although with age this difference is not so pronounced. But what is more important, the type of failure undergoes a definite change. Where all the surfacing material has been sanded off, the type of failure is one of crumbling away at point of impact. When increasing quantities of surfacer are left over the primer, the type of failure changes to one in which large areas on each side of point of impact are shattered cleanly off to the base metal (Figure 2).

The effect of surfacing coats on the distensibility of an otherwise flexible system is even more severe. Systems without surfacer, which show an initial distensibility of greater than 17.7 per cent, fall immediately to less than 3 per cent when surfacer is left between primer and color enamel. Furthermore, the adhesion of the system to the base metal suffers. It is surprising that on bending, the entire system should peel away from the base metal, since the primer itself exhibits excellent adhesion and high per cent elongation. The explanation is probably as follows:

The inflexible and relatively very thick surfacing layer has excellent adhesion to both the primer and color enamel. When

Table VIII. Service Tests on Trucks

Finish System	Materials Used	No. of Trucks	Kind of Trucks	Exposure Location	Service Life (Months)	Type of Failure
C	P—218 E—102	2	1 Composite 1 All metal	North	30–36	Chalked mostly. Some wood grain failure
C	P—218 E—102	2	1 Composite 1 All metal	Florida	30–36	Chalked mostly. Some wood grain failure
E	P—216 E—116	2	All metal	North	24–36	Chalked mostly. Some checking and cracking
E	P—216 E—116	2	All metal	Florida	15–18	Most checking and cracking. Severe chalking
F	P—206 E—106	3	All metal	North	12–18	Very severe chalking
F	P—206 E—106	1	All metal	Florida	9–12	Very severe chalking. Slight checking
G	P—216 E—207	6	4 Composite 2 All metal	North	24–36	Mostly checking. Wood grain failure
G	P—216 E—207	2	Composite	Florida	18–24	Severe chalking. Checking. Wood grain failure
H	P—206 E—206	3	Composite	North	15–17	Checking. Wood grain failure
H	P—206 E—206	1	Composite	Florida	9–12	Checking. Wood grain failure
J	P—218 E—304	1	All metal	North	36+	Still in service
J	P—218 E—304	2	1 Composite 1 All metal	Florida	30+	Still in service

Table IX. Effect of Surfaces

	No. of Coats	Wear				Impact				Mandrel			
		Set I		Set IV		Set I		Set IV		Set I		Set IV	
		W[a]	T[b]	W	T	R. p. m.	End point[c]	R. p. m.	End point[c]	Elong. %	Adhesion	Elong. %	Adhesion
Lacquer type													
P—211	1	32	1.27	38	0.76	430	1	<400	1	>17.7	Good	3.9	Fair
E—103	2	58	2.03	53	1.78								
P—211	1	24	1.02	58	0.76								
S—102	1	38	2.03	32	2.79	550	2	480	2	5.7	Good	<3	Poor
E—103	2	54	2.03	76	1.27								
P—211	1	38	1.02	49	1.27								
S—102	1	38	2.54	47	2.03	430	3	670	3	<3	None	<3	None
G—101	1	24	3.56	34	3.30	(To primer)							
S—102	1	36	2.29	39	2.79								
E—103	2	52	2.54	71	1.52								
Oil type													
P—216	1	25	0.76	53	0.76	700	1	800	1	>17.7	Good	7.4	Good
E—207	2	58	2.03	63	1.78								
P—216	1	31	1.02	43	1.02	1080							
S—201	1	22	5.59	29	4.06		1	700	2	3.9	Poor	<3	Poor
E—207	2	45	2.03	65	1.52	640							
P—216	1	30	1.52	45	1.02								
G—201	1 }	33	6.35	32	6.35	>1500	3	700	2	3.9	Poor	<3	Poor
S—201	1 }												
E—207	2	48	2.79	64	1.78								
P—218	1	28	1.27	46	0.76	550	2	465	2	>17.7	Fair	<3	None
E—304	2	73	2.03	76	1.52								
Synthetic type													
P—218	1	31	1.78	46	1.52								
S—301	1	22	6.10	26	6.35	1300	2	555	2	<3	Fair	<3	None
E—304	2	70	2.03	83	1.52								
P—218	1	34	1.78	37	1.27								
G—301	1	36	4.06	32	1.79	1020	3	710	3	<3	Fair	<3	None
S—301	1	23	6.35	26	6.86								
E—304	2	61	2.29	90	1.52								

[a] Grams Carborundum to abrade through 2.54×10^{-3} cm. (0.001 inch) of coating.
[b] Thickness, in 10^3 cm.
[c] 1, Crumbling away at point of impact, no shattering; 2, medium shattering around point of impact; 3, serious shattering around point of impact.

such a system is subjected to a bending stress, the surfacing coat tends to remain in a straight plane. The adhesion of the flexible coats to this surfacer inhibits their motion, setting up stresses at the primer-metal interface sufficient to overcome the adhesional bond at this point. Thus, on bending, a point is soon reached where the breaking strength of the surfacer is surpassed; at this instant the whole system must bend over a very sharp radius and the distensibility of the primer and color coats is exceeded. In other words, even though the system has lost distensibility and adhesion, actually the primer may be unaltered in these properties, the adhesion to the surfacer merely bringing about a condition of stress which even the best primer cannot withstand. Figure 3 illustrates the point.

Conclusion

Although the use of this method of testing has proved of definite economic value to the consumer, since it is less time-consuming and more informative than exposure and simulated service testing, its real value lies in the hands of the manufacturer, who by its use would materially speed up the formulation of improved finishing materials.

The importance of attempting to arrive at a quantitative measurement of the underlying properties in which the durability and serviceability of a finish may be defined cannot be overemphasized. The tests that have been described are probably not the last word of development. However, it is felt that a wide adoption of test procedures such as described would prove a real boon to the paint industry.

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Correction

In the article by Ball, Schmidt, and Bergstresser entitled "New Type of Antimony Electrode for pH Measurements" [Ind. Eng. Chem., Anal. Ed., 6, 60 (1934)] in line 12 the equation of Parks and Beard for the antimony electrode was given as "$E = -0.007 + 0.05195$ pH at 25°." This should read "$E = -0.007 + 0.05915$ pH at 25° when measured against a saturated calomel electrode."

T. R. Ball, W. B. Schmidt, and K. S. Bergstresser

Significance of Solvent Extraction and Rational Analysis in Coal Carbonization

Reproducibility of Analytical Results

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FOR a number of years considerable attention has been given to the resolution of coal by means of solvents. That the coking principle is related to the extractable matter in coal is unquestionably true, as it is possible to deprive a coal of its coking powers by solvent action and to restore them to a degree by reincorporating the extract. The exact nature of the relationship, however, is still but poorly understood. Hypotheses have been made and apparently substantiated, only to be destroyed later by conflicting evidence. Recently the use of rational analysis has been emphasized by Francis (*11*) as an aid to determining the field of usefulness for a particular coal, but this view is disputed by Roberts (*14*).

At the time the Pittsburgh Experiment Station of the United States Bureau of Mines undertook a survey of the gas-, coke-, and by-product–making properties of American coals, it was decided to include among the many tests and analytical procedures to be investigated an assay of the bituminous material extractable by benzene under pressure (*10*) including a separation into oily and solid bitumens, a resolution of the coal into its alpha, beta, and gamma constituents according to Wheeler (*13*, *16*), and an analysis of the so-called rational constituents of coal—namely, the total bitumens, ulmins, and resistant plant residues (*12*).

The end in view was the establishment, if possible, of some quantitative relationships between the amounts of such extracts or "rational" ingredients and the gas-, coke-, and by-product–making properties of the coal or other functions of the coal numerically expressible. Attempt has been made to carry out these extractions and separations according to procedures that would reduce variables to a minimum.

Twenty coals (Table I) were studied exhaustively and data compiled for a comparison with such properties as ultimate and proximate analysis, behavior on carbonization, and yields and properties of the coke and by-products. To complete the comparison, certain specimens were resampled and reanalyzed to ascertain the duplicability of these tests. Split samples have been analyzed by different laboratories to see if the personal equation is significant in this type of analysis.

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Alpha, Beta, and Gamma Determination

The resolution of coal into alpha, beta, and gamma constituents after Wheeler (*13*, *16*) involves the extraction of coal in a Soxhlet apparatus with pyridine over a period of days, the isolation of the pyridine extract which is made up of both beta and gamma constituents, and the separation of these two by another Soxhlet extraction with chloroform. Table II summarizes the analyses for these constituents as well as the values for bitumens, ulmins, and resistant residues.

The operations for separating coal into alpha, beta, and gamma constituents, simple though they may appear superficially, present difficulties. Coals vary, for example, in the length of time required to extract them fully. Some give up their soluble matter quickly; others require long periods. Ground coal in a paper Soxhlet thimble tends to swell and even tear it apart, provided an inert diluent is not used. The particles may disintegrate under the action of pyridine or may become extremely friable. At any rate, indications are that the penetration by pyridine is extremely deep. The chief drawback to the pyridine extraction is the difficulty of obtaining check results on split samples, despite every effort to inhibit oxidation and to insure uniformity in the conditions, as has been repeatedly observed by every worker who has attempted pyridine extraction of coal. The chloroform extraction of the pyridine extract proceeds with greater ease and with less variability in the amount of material separated.

Procedure. As the technic of the alpha, beta, and gamma determination became better standardized and as improvements were incorporated into the Soxhlet apparatus, it was found possible to obtain closer checks than in the preliminary tests.

Table I. Description and Analyses of Coals

Coal No.	State	County	Mine	Bed	Ultimate Analysis, Moisture- and Ash-Free: Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur	Proximate Analysis, Moisture- and Ash-Free: Volatile matter	Fixed carbon
					%	%	%	%	%	%	%
1	Pennsylvania	Allegheny	Ocean No. 2	Pittsburgh	5.6	84.6	1.7	7.0	1.1	36.7	63.3
2	Kentucky	Letcher	No. 204	Elkhorn	6.1	84.6	1.6	7.1	0.6	38.3	61.7
3	Virginia	Wise	Roda No. 3	Taggart	6.0	86.3	1.6	5.5	0.6	37.8	62.2
4	Maryland	Garrett	Arnold	Davis	5.4	87.5	1.7	3.7	1.7	24.9	75.1
5	60 per cent No. 4; 40 per cent No. 1										
6	20 per cent No. 4; 80 per cent No. 1										
7	Alabama	Jefferson	Flat Top	Mary Lee (unwashed)	5.4	86.2	1.8	5.7	0.9	33.6	66.4
8	Alabama	Jefferson	Flat Top	Mary Lee (washed)	5.3	87.1	1.8	4.9	0.9	31.5	68.5
9	Pennsylvania	Fayette	Edenborn	Pittsburgh	5.5	85.5	1.8	6.1	1.1	37.1	62.9
10	Illinois	Franklin	Orient No. 1	No. 6	5.3	82.2	1.7	9.8	1.0	40.3	59.7
11	British Columbia		Michel	Nos. 2 and 3	5.1	87.4	1.4	5.5	0.6	29.2	70.8
12	Pennsylvania	Fayette	Allison	Pittsburgh	5.7	85.1	1.8	6.0	1.4	37.1	62.9
13	Alabama	Walker	Empire	Black Creek	5.7	84.0	1.9	7.2	1.2	38.2	61.8
14	W. Virginia	Logan	Boone No. 2	Chilton	5.5	84.8	1.7	7.4	0.6	38.7	61.3
15	W. Virginia	Kanawha	Point Lick No. 4	No. 2 gas	5.6	84.2	1.5	7.8	0.9	40.6	59.4
16	W. Virginia	Boone	Spruce River No. 4	Alma	5.7	84.5	1.6	6.3	1.9	41.5	58.5
17	Alabama	Jefferson	Wylam No. 8	Pratt (unwashed)	5.4	86.4	1.8	5.7	0.8	33.7	66.3
18	Alabama	Jefferson	Wylam No. 8	Pratt (washed)	5.5	86.8	1.8	5.3	0.6	33.6	66.4
19	Utah	Carbon	Columbia	Lower Sunnyside	5.8	81.5	1.7	9.9	1.1	43.4	56.6
20	Pennsylvania	Allegheny	Wildwood	Thick Freeport	5.7	84.0	1.7	7.2	1.4	39.6	60.4

Table II. Results of Extraction with Solvents and Rational Analyses. (Ash-free dry basis, original samples)

Coal No.	Bed	Alpha	Beta	Gamma	Bitumens	Ulmins	Resistant Residues
		%	%	%	%	%	%
1	Pittsburgh, Ocean No. 2 (unpublished)	63.9	18.8	17.3	11.9	82.1	6.10
2	Elkhorn (unpublished)	68.6	17.5	13.9	10.0	84.6	5.5
3	Taggart, Roda (*3*)	71.1	17.6	11.3	11.0	79.5	9.5
4	Davis, Upper Freeport (*1*)	93.7	2.1	4.2	9.4	84.9	5.7
5	Blend of 80 per cent Pittsburgh and 20 per cent Davis coals	..	..	..	..	..	..
6	Blend of 60 per cent Davis and 40 per cent Pittsburgh coals	..	..	..	..	..	..
7	Mary Lee (unwashed, *4*)	62.0	26.7	11.3	16.2	69.5	14.3
8	Mary Lee (washed, *4*)	65.7	15.0	19.3	11.2	77.6	11.2
9	Edenborn, Pittsburgh (*5*)	62.2	26.5	11.3	14.3	76.9	8.8
10	No. 6 (Franklin Co., Ill., *6*)	73.3	19.3	7.4	6.3	87.5	6.2
11	No. 3 (Michel, B. C., *2*)	72.5	14.7	11.8	8.9	82.2	8.9
12	Allison, Pittsburgh (*2*)	64.0	20.0	16.0	13.9	69.7	16.4
13	Black Creek (*7*)	75.1	15.3	9.6	9.9	71.3	18.8
14	Chilton (*3*)	68.4	17.3	14.3	11.7	70.3	18.0
15	No. 2 gas (*9*)	75.0	14.6	10.4	11.0	78.5	10.5
16	Alma (unpublished)	71.0	15.8	13.2	14.8	75.2	10.0
17	Pratt (unwashed, unpublished)	68.9	14.3	16.8	13.8	73.7	12.6
18	Pratt (washed, unpublished)	70.0	15.0	15.0	12.5	79.5	8.0
19	Lower Sunnyside (unpublished)	73.6	15.2	11.3	11.3	74.9	13.8
20	Thick Freeport (unpublished)	69.8	20.4	10.7	12.5	70.7	16.7

A representative laboratory sample of the coal is ground to pass a 60-mesh sieve and dried for 1 hour at 105°C. One to 1.5 grams are mixed with 4 or 5 volumes of clean quartz sand in an alundum Soxhlet thimble and extracted with 125 cc. of pure pyridine in an atmosphere of dry nitrogen. The major portion of soluble material is removed in 4 to 6 hours, but appreciable additional amounts are often obtained up to 72 hours. This is the minimum time allowed regardless of the rapidity of the extraction and usually is sufficient for the typically bituminous coals. When coals difficult to extract are encountered, as is evidenced by the persistence of color in the descending solvent, an even longer time may be required. In general, the extraction is continued 24 hours after the descending solvent has turned colorless. Beyond this point, an additional 24 hours' extraction, as a rule, removes only slight amounts (0.2 to 0.3 per cent) of soluble material.

The type of Soxhlet best adapted to this extraction is one equipped with standard ground-glass joints. In the event of breakage any part can be replaced readily from stock; furthermore, a goose-neck can be constructed from standard joints for use in distilling off the pyridine from the extract at the end of the operation. Thus, cork and rubber connections, which are attacked appreciably by pyridine, are eliminated.

Dry nitrogen is admitted to the apparatus in a slow stream through a capillary side arm sealed to the extraction flask well above the surface of the boiling liquid. Between the tank and drying tower, a rubber gas-storage bulb, such as is used in an Orsat apparatus, is inserted on a T-connection, to maintain a steady flow of gas at all times. From the top of the condenser, nitrogen is allowed to escape through a sulfuric acid seal so constructed that when the Soxhlet spills, a sufficient volume of acid rises into a reservoir to compensate for the partial vacuum created.

During the initial part of the extraction, the Soxhlet should be run slowly, about one spill every 10 or 15 minutes, to prevent the alundum thimble, which does not drain very rapidly during the first hour, from overflowing. Subsequently, the operation may be speeded up until the spills occur every 5 to 7 minutes, provided the porosity of the thimble is not too fine.

After the first 7 or 8 hours of extraction, it is advisable to substitute fresh pyridine, as protracted boiling of the somewhat concentrated solution of coal extract tends to polymerize it in part, and at the end of 48 hours the solvent should be changed again for the same reason. After 24 hours' extraction with the third increment if the color of the solution is of deep orange or darker, it is advisable to continue the extraction for another 24 hours. Meanwhile the accumulated fractions are set away, tightly stoppered, in a single container.

The combined solutions of beta and gamma compounds are concentrated to a small volume (10 or 15 cc.) on a sand or mineral-oil bath and then poured slowly, with stirring, into a beaker containing 200 to 300 cc. of dilute hydrochloric acid to remove remaining pyridine. A quantitative transfer is accomplished by carefully washing the flask two or three times with a little fresh pyridine. The mixture is then heated to boiling and allowed to cool before filtering through a tared filter crucible with an integral porous bottom of fritted glass. The filtrate is discarded. The residue in the form of a sticky cake is carefully triturated in the crucible with distilled water by means of a rubber policeman. To avoid the formation of lumps, which will not otherwise disperse, the water is added a little at a time until the mixture has acquired the consistency of thin batter.

The mixture is washed back into the beaker by means of a stream of water from a wash bottle, heated to boiling, and filtered as before through the same crucible. This operation is repeated once again and the crucible dried for 12 hours in a vacuum over sulfuric acid. It is then weighed. By subtracting the tare of the crucibles the weight of beta and gamma constituents is obtained.

The dry cake is crushed to a powder with a stirring rod and as much of it as possible transferred to a paper Soxhlet thimble. The remainder of the beta and gamma compounds adhering to the sides and bottom of the crucible is transferred almost quantitatively by repeated washing with small increments of chloroform, scrubbing with a policeman, and pouring the mixture through the thimble already in position in the extractor. Finally warm chloroform is passed through the disk by suction or by blowing to remove any gamma compound which may have found its way into the pores. In all 100 to 125 cc. of chloroform are used. (The extraction is carried out in an atmosphere of nitrogen exactly as in the case of the pyridine, until no further coloration is produced in the descending solvent.) After the first 7 or 8 hours the extraction is continued with fresh chloroform and after 12 or 24 hours with a third quantity of fresh chloroform. This is repeated until the solution after 8 hours is only slightly colored. The speed of extraction is maintained at a considerably higher rate than with pyridine. The combined solutions are evaporated from the previously tared extraction flask to a small volume on the water bath, 10 cc. of petroleum ether are added, very carefully evaporated to dryness, and the final traces of solvent are removed by reducing the pressure with a water pump.

Table III. Deviations from Mean

Coal No.	Alpha	Beta	Gamma
	%	%	%
1	0.05	0.30	0.25
2	0.40	0.10	0.30
3	0.40	0.67	0.27
4	0.15	0.20	0.35
7	0.30	0.45	0.15
8	0.45	0.85	0.40
9	0.14	0.48	0.62
10	0.05	0.45	0.40
11	0.50	0.85	0.35
12	0.15	0.05	0.20
13	0.05	0.25	0.20
14	0.50	0.30	0.20
15	0.40	0.30	0.10
16	0.50	0.05	0.55
17	0.65	0.70	0.05
18	0.30	0.55	0.25
19	0.65	0.35	0.30
20	0.35	0.15	0.20
S-3	0.00	0.45	0.45
S-4	0.75	0.55	0.20
S-5	0.45	0.10	0.35
S-6	1.05	0.75	0.30
S-7	0.85	0.80	0.05
S-8	0.80	0.70	0.10
S-9	0.00	0.35	0.35
S-10	0.40	0.25	0.15
Av.	0.40	0.42	0.27

The weight of residue after thorough drying represents the amount of gamma compounds and is subtracted from the sum of the beta and gamma previously obtained; the difference, minus the ash content of the beta compounds, gives the amount of beta compounds in the original coal sample. The gamma group contains virtually no ash. Calculations of the true percentages of beta and gamma groups are based upon the ash-free dry coal. The alpha group is determined by the

difference between 100 and the sum of the beta and gamma groups.

Table III brings out the deviations from the mean of 26 duplicate determinations, which were in most cases run side by side.

It will be noted that the deviations from the mean, particularly of the alpha, vary within wide limits. For sample S-3 we find a 0 deviation but for S-6 a value of 1.05. S-7 also has a high one, 0.85. The same is true of the beta, where it is even more significant because of the relatively small quantities, compared with the alpha. Here we find two with deviations from the mean of 0.85 per cent (8 and 11) and one of 0.8 (S-7). The gamma apparently checks out a little better, the maximum being 0.62 (9) and the next highest, 0.55 (16).

Benzene-Pressure Extraction

The benzene-pressure extraction has been carried out in a Fischer-type apparatus (*10*) at a temperature of 280° C. and a pressure of 43 atmospheres. (The critical temperature and pressure of benzene are 288.5° C. and 47.7 atmospheres, respectively.) Coal is extracted repeatedly under these conditions until the increment of extract amounts to less than 0.3 per cent of the coal substance. The cooled benzene solution is filtered (to remove precipitated bitumens), and the filtrate is distilled to remove benzene. The residual matter is separated into oily and solid bitumens by dissolving 5 grams in 15 cc. of benzene and stirring into 50 cc. of petroleum ether. The precipitate formed is termed "solid bitumens" and the dissolved substance, "oily bitumens." In this paper no consideration will be given to the role of the oily and solid bitumens individually but only to the bitumens as a whole, in relation to other critical data on the respective coals. Table II lists the total bitumen content of the coals studied.

The duplicability of this determination is brought out by Table IV, which lists the deviation from the mean for 12 coal samples on which duplicate determinations were made.

Table IV. Deviations from the Mean, Benzene-Pressure Extract

Coal No.	Deviation
	%
7	0.2
14	0.3
15	0.35
16	0.2
17	0.5
S-9	0.25
19	0.3
S-3	0.0
20	0.05
21	0.45
22	0.25
22a	0.1
Av.	0.25

The average deviation, 0.25, is almost identical with the average deviation for the gamma, and, the authors think, represents a fair duplicability for this type of analysis. The largest variation is 0.45 (sample 21).

Ulmins and Resistant Residues

The residual coal from the benzene-pressure extraction was used to obtain the relative proportion of ulmins and resistant residues. In using this material the authors were slightly at variance with the Wheeler school (*12*) which recommends the residue from the pyridine extraction for this determination, but they adopted the procedure not without good reason, the chief being the contamination of pyridine-extracted coal with sand.

Despite the heat treatment of the coal at 280° C., the ulmins were found quite as readily regeneratable to humic acids as are the ulmins of a pyridine-treated coal, and furthermore, the residual spores and cuticular matter are maintained in an excellent state of preservation.

Ulmins were obtained by oxidizing the bitumen-free coal for a specific time with various strengths of dilute nitric acid containing (or not containing) potassium chlorate. The detailed procedure follows:

The residual coal from the benzene-pressure extraction is either air-dried for several hours or heated at 105° C. under a high vacuum for 2 or 3 hours to remove the excess benzene, and then ground to pass a 20-mesh sieve. A 10- or 15-gram representative sample is taken and ground further to pass a 150-mesh sieve. During this process the coal is screened frequently to avoid an excessive formation of fines. The fines are not discarded. The specimen is then heated at 105° C. to constant weight.

Three or four 0.5-gram samples of the treated coal are refluxed 7 hours with such of the oxidizing solutions in Table V as are in the vicinity of the one recommended for a coal of its rank. On cooling, each is filtered through a filter-crucible (tared at the end of the analysis rather than prior to the analysis because of the loss in weight caused by the caustic potash) with an integral porous bottom of fritted glass and washed well with cold water. The pores of the disks should be very fine to minimize the possibility of finely divided solid material passing through. This detail is especially important at a later stage of the analysis when the residues are being separated from the caustic humate solutions.

Table V. Oxidizing Solutions

Carbon Content of Coal, Moisture- and Ash-Free Basis	Oxidizing Solutions			
	N HNO_3	2 N HNO_3	Water	$KClO_3$
	Cc.	*Cc.*	*Cc.*	*Grams*
78	37.5	..	12.5	Nil
79	40	..	10	Nil
80	42.5	..	7.5	Nil
81	45	..	5	Nil
82	47.5	..	2.5	Nil
83	50	..	Nil	Nil
84	46 and	4	Nil	Nil
85	..	28	22	0.2
86	..	29	21	0.35
87	..	30	20	0.5
88	..	32.5	17.5	0.625
89	..	35	15	0.75
90	..	40	10	1.0
91	..	50	Nil	1.5

The residue from one sample is washed from the crucible into an Erlenmeyer flask by 100 cc. of distilled water. Twenty cubic centimeters of N potassium hydroxide are added and the mixture is refluxed gently for 1.25 hours, during which time the regenerated humic acids go into solution as potassium humates. The refluxed mixture is centrifuged for 10 minutes in thick-walled 250-cc. Pyrex glass bottles, especially adapted for this purpose to throw down all finely suspended matter that otherwise would hinder the filtration. As much as possible of the supernatant liquid is siphoned off very slowly through the same fritted glass crucible as was used above, and the remaining liquid containing more or less sludge is decanted into a small beaker and set aside to be filtered later. The solid cake remaining in the thick-walled bottle is returned to the Erlenmeyer flask, treated with an additional 50-cc. portion of 1 per cent potassium hydroxide, heated to the boiling temperature for 0.5 hour, and the process of separating solid material from the solution is repeated. The sludges from both the first and second treatments now are united and filtered, after which the total residual matter is washed into a beaker with distilled water.

The correct degree of oxidation is determined microscopically. An over-oxidized coal will be manifest by a more or less frayed and bleached condition of the spores and cuticular matter. An underoxidized sample will contain masses of dark humic matter. For this reason it is necessary for the operator to judge carefully between them and select that sample which has had the proper oxidation for the determination. The mixture in the beaker representing the one thus selected accordingly is acidified with hydrochloric acid to expedite the filtration, brought to the boiling point, and filtered through the same tared crucible used above. The residues are transferred quantitatively and washed with hot water. Drying is carried out at 105° C. for 1 hour and then in a desiccator over sulfuric acid or calcium chloride to constant weight. The weight of residues thus obtained is calculated to a true value by determining the ash content. As the amount of residues necessarily is small, this determination requires the

use of semi-micromethods (20 to 40 mg.). Calculation of the residues to an ash-free dry basis is made by using the following equation:

$$R = \frac{100y(1-c)(1-b)}{x(1-a)}$$

where x = weight of dry sample (free of bitumens)
y = weight of residue after extraction with alkali
$a = \frac{\text{per cent of ash in coal before extraction with benzene}}{100}$
$b = \frac{\text{per cent bitumens of ash-containing coal}}{100}$
$c = \frac{\text{per cent of ash in residues}}{100}$

If the microscopic examination leaves some room for doubt, an additional procedure is followed. Four more determinations of residues are made in which each oxidizing solution employed contains exactly the proportion of potassium chlorate found to give the best degree of oxidation. The amounts of 2 N nitric acid, however, are varied. The residues after the alkali treatment subsequently are plotted against the corresponding volumes of nitric acid. If a sharp break occurs in the curve, the "heel" is selected (below which the curve is almost horizontal) as representing the point of complete ulmin regeneration. If a smooth curve results, resort must again be made to the microscope for selecting the proper point.

The percentage of ulmin in the original coal, on the ash-free dry basis, is calculated by subtracting the sum of the bitumens and resistant plant residues from 100.

The oxidations of the extracted coals usually were not run in duplicate on account of the number that were necessary to establish the curves. That a fair degree of duplication can be expected is learned from Table VI, which shows the amount of residual matter from an original sample and a resample obtained by treating each with identical amounts of oxidizing reagent and extracting the humic acids with alkali.

Table VI. Regeneration of Humic Acids

(Oxidation of original and resamples)

Coal	Oxidizing Mixture: Potassium chlorate	Oxidizing Mixture: 2 N nitric acid	Residues from Original Sample	Residues from Resample
	G./0.5-g. sample	*Cc./0.5-g. sample*	%	%
Pratt	..	..	...	..
	0.35	25.0	13.86	12.4
	0.35	30.0	12.5	11.3
	0.35	35.0	...	10.1
	0.35	40.0	11.19	9.2
Lower Sunnyside	..	..	...	..
	0.0	16.0	13.8	14.0
	0.0	20.0	11.9	12.9
	0.0	24.0	10.3	12.3
	0.0	28.0	...	11.1
Pittsburgh (Monongah)	0.5	20.0	9.7	..
	0.5	25.0	8.5	9.0
	0.5	30.0	7.1	7.7
	0.5	35.0	6.7	7.3
	0.5	40.0	6.6	6.9

Average deviation from mean of 10 pairs of oxidation residues from original samples and resamples, 0.49.

The average deviation from the mean of 0.49, of course, is obtained not from a series of duplicate determinations but from pairs made up of an original and a resample and hence is the result not only of experimental error but also of aging effects on the resample and possible sampling errors. It is seen that the deviation is not consistently of the same sign. The residual matter from the resamples of the Lower Sunnyside and Monongah seem to be higher than for the original samples but vice versa for the Pratt.

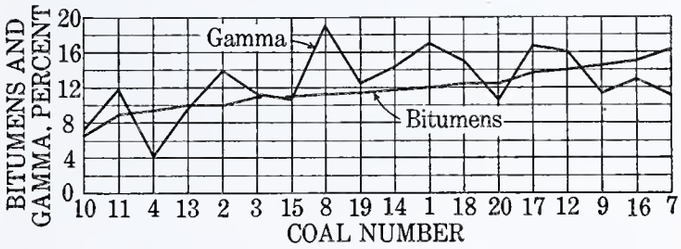

Figure 1. Relation of Bitumens to Gamma

At the conclusion of this study, four of the coals were resampled and independent solvent extraction tests and rational analyses carried out on the resamples. The results are shown in Table VII, together with the results on the original samples for comparison.

The deviations, it will be noted, are somewhat larger than are obtained on split samples analyzed side by side (Tables III and IV). Moreover, the variations are not always in the same direction on proceeding from the original to the resample. Therefore it is not permissible to generalize on the effects of aging.

Table VIII. Rational Analysis by Two Different Laboratories

Coal	Laboratory	Hydrocarbons and Resins[a]	Deviation from Mean	Resistant Residues	Ulmins
Davis	Laboratory A	0.6		Less than 1	98.4
	U. S. Bureau of Mines	1.7	0.55	5.5	92.8
Edenborn	Laboratory A	6.5	0.0	5.0	88.4
	U. S. Bureau of Mines	6.5		8.6	84.9
Mary Lee (washed)	Laboratory A	5.0	1.0	2.0	93.0
	U. S. Bureau of Mines	7.0		7.8	85.2
Orient	Laboratory A	5.5	0.05	4.0	90.5
	U. S. Bureau of Mines	5.6		9.9	84.5
Av.			0.4		

[a] Material extracted by refluxing sample with pyridine and extracting pyridine extract with ether.

An attempt was made to bring out the duplicability of the solvent and rational analysis by two laboratories. The authors succeeded in interesting another laboratory to the extent of carrying out a rational analysis on four split samples under fixed conditions, but have not done so on the alpha, beta, and gamma separations nor the benzene-pressure extraction. The results are listed in Table VIII.

Exeept in the case of the Davis, a most difficultly extraetable coal, the agreement for hydrocarbons and resins is fair.

Table VII. Solvent Extraction and Rational Analysis

(Original and resamples)

Sample	Date of Sampling	Alpha	Beta	Gamma	Bitumens	Ulmins	Resistant Residues
Sunnyside	Original, 4–15–32	73.55	15.15	11.3	11.3	74.9	13.8
	Resample, 8–25–32	75.2	13.55	11.25	9.9	76.1	14.0
Thick Freeport	Original, 6–22–32	69.8	20.4	10.7	..	..	..
	Resample, 8–25–32	68.0	18.9	13.1	..	..	..
Pratt	Original, 2–4–32	68.9	14.3	16.75	13.8	73.7	12.5
	Resample, 11–10–32	68.6	16.55	14.85	11.5	77.2	11.3
Pittsburgh (Monongah)	Original, 11–16–32	67.0	18.75	14.25	14.8	78.1	7.1
	Resample, 12–23–32	65.35	19.75	14.9	13.7	78.6	7.7
	VARIATION FROM MEAN OF ORIGINAL AND RESAMPLE						
Sunnyside		0.83	0.80	0.03	0.7	0.6	0.1
Thick Freeport		0.90	0.75	1.30	..	..	..
Pratt		0.15	1.28	0.95	1.15	1.80	0.65
Pittsburgh (Monongah)		0.73	0.45	0.32	0.55	0.25	0.30
Av.		0.65	0.82	0.65	0.80	0.88	0.35[a]

[a] The value of 0.53 computed from 10 oxidation tests (*q. v.*) is probably more significant than the value of 0.35 on the 3 oxidation tests of the table taken as the actual values of resistant residues.

The figures for resistant residues, on the other hand, were puzzling at first, but it was learned later that Laboratory A had used a medium-porosity filtering disk for separating these residues from the potassium humate solution, while the authors had used a fine-porosity disk. The strength of oxidizing solution used for regenerating the ulmins was identical in the two laboratories. The conclusion was that a portion at least of the resistant residues must have passed through the filter in Laboratory A and been reported as ulmins. Such being the case, the variations from the mean of the values for resistant residues and ulmins are not significant, although the values for hydrocarbons and resins are comparable. The variations from the mean of the values obtained by Laboratory A and the U. S. Bureau of Mines for these constituents also are shown in this table. The average deviation of 0.4 computed from four samples is only slightly greater than the average obtained in the Bureau of Mines laboratory on duplicate samples.

A comparison of four representatives coals from the Pittsburgh bed has proved interesting. Those studied were Ocean No. 2 from Allegheny County, Pa., Edenborn from Fayette County, Pa., Allison from Fayette County, Pa., and Monongah from Marion County, W. Va. The solvent extraction and rational analysis for these coals are summarized in Table IX.

Table IX. Solvent Extraction and Rational Analysis, Pittsburgh Bed Coal

Coal	Alpha	Beta	Gamma	Bitumens	Ulmins	Resistant Plant Residues
Ocean No. 2	63.9	18.8	17.3	11.85	82.05	6.10[a]
Edenborn	62.2	26.5	11.3	14.3	76.9	8.80[a]
Allison	64.0	20.0	16.0	13.9	69.7	16.40[a]
Monongah	68.0	17.8	14.2	14.8	78.1	7.10[a]

[a] Correspond to oxidations with same oxidizing solution.

Here we observe notable similarities in the alpha, beta, and gamma of the Ocean and Allison. The bitumens are also fairly close together, but the resistant plant residues and ulmins are both significantly different. The total beta plus gamma is quite similar for three (the Ocean, Edenborn, and Allison), but it is low for the Monongah.

The resistant residues, it is interesting to note, were all obtained by using the same strength and make-up of oxidizing solutions to regenerate the ulmins.

Significance of Coal Constituents in Coal Carbonization

It was attempted to correlate the data of Table II with as many other properties of the coals, numerically expressible, as might conceivably bear a relationship. A comprehensive table was drawn up containing all values for the rational extraction and solvent analysis tests, and in addition, for fixed carbon, carbon-hydrogen ratio, volatile matter, coke-hardness factor at 500° and 900° C. carbonizing temperature, initial contraction temperature, plastic range, gas yield at 500° C. carbonizing temperature, tar and light-oil yield, agglutinating index, swelling coefficient, coke stability (900° C., tumbler on 2.54 cm.), and coke shatter (900° C. on 3.81 cm.). Columns were set up of ratios of solvent extraction and rational analysis data to every other listed property of the coal or its products of carbonization. This table proved a disappointment in that none of the ratios exhibited any degree of constancy through the series.

Fifty-three curves were plotted in which the verticals from left to right represented the different coals in the ascending order of the beta, gamma, bitumens, or ulmins, other numerical values being plotted on the same verticals and the adjacent points connected by lines. These again were a disappointment from the standpoint of the lack of relationship that was so clearly evident in most cases. For the beta and

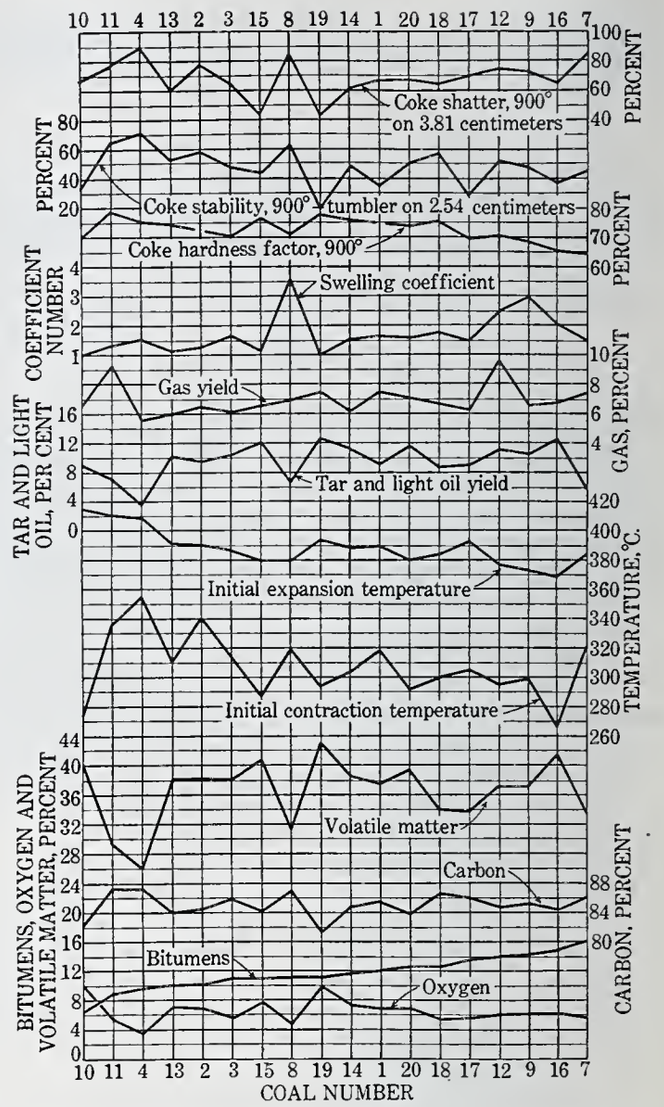

Figure 2. Relation of Bitumens to Other Properties of Coal and Coke

ulmins, no correlation at all could be deduced and for the bitumens and gamma, only a few curves seemed to bring out relationships. These are of the most general kind subject to interpretation and qualification. Exceptions to the rule are numerous.

The first of these curves, Figure 1, shows the gamma plotted against the bitumens. As previous work had shown the gamma and bitumens to be on the same order of magnitude, the authors anticipated that the percentages of these two would closely parallel one another, the gamma possibly being slightly greater. That such is not the case is very evident from these curves, although the general direction of both is upward. Nevertheless the fluctuations are too numerous to warrant drawing conclusions. Portions of both the gamma and bitumens are undoubtedly identical, while certain other portions must be dissimilar, as it is possible to extract a benzene-extracted coal further with pyridine, and a pyridine-extracted coal with benzene. This fact doubtless accounts for the fluctuations.

Figure 2 shows a set of curves in which various values are plotted against the bitumens in the ascending order of bitumens. Some of these show no relationship at all but are included merely because they are functions of particular interest to the coal chemist.

The general lack of relationship is evident from a casual glance at the curves. Oxygen, carbon, volatile matter, tar and light oil, and swelling coefficient show no relationships at all to bitumens. Coke-hardness factor at 900° C. has a

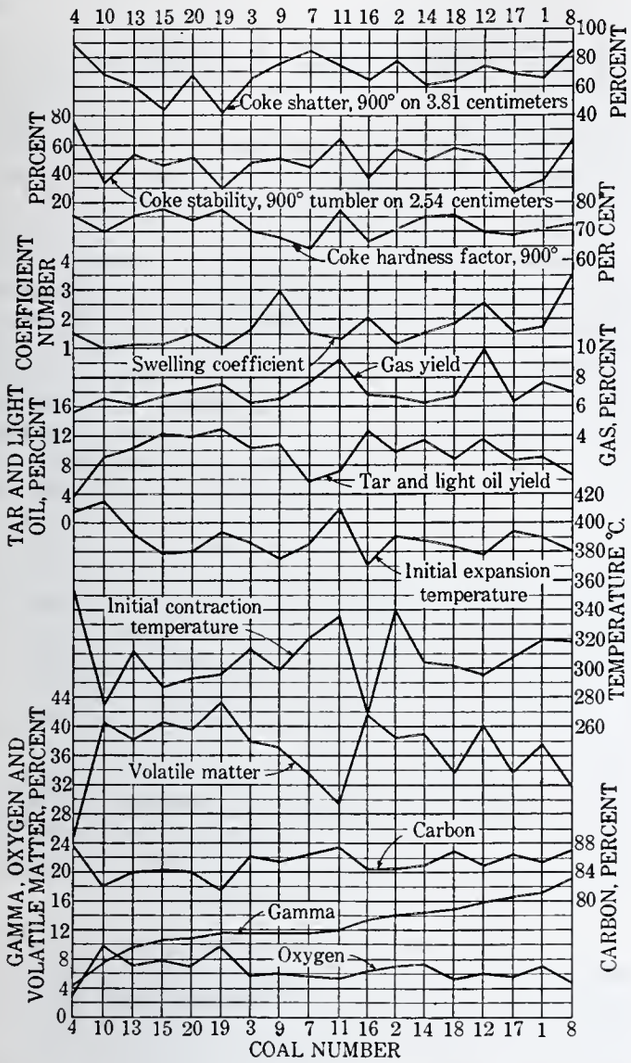

FIGURE 3. RELATION OF GAMMA TO OTHER PROPERTIES OF COAL AND COKE

rather persistent downward inclination with rising bitumens with but few exceptions. The initial expansion temperature curve is more satisfactory still from this standpoint, as it shows a fairly smooth decline with increase in bitumens. The initial contraction temperature likewise is downward, but the fluctuations are wide. Coke-stability factor (900° C.) shows a general tendency to decline with bitumen increase, though the descent is not at all regular. Values for the coke-shatter test (900° C. on 3.81 cm.) on the other hand appear to descend almost to the midpoint and then to rise. Neither of these two curves will permit drawing definite conclusions.

Figure 3 shows the curves for the same functions plotted against gamma values in the ascending order of gamma. Oxygen appears to fall slightly with increase in gamma. This property is in accord with the recent findings of Shimmura (*15*), who, however, has studied many more high-oxygen coals than are included here and has been able to generalize better for this reason.

The carbon content rises slightly with the gamma, but the volatile matter tends to go down. Notable deviations in the case of the volatile matter are found for coals Nos. 4 and 11. No. 4 is a semi-bituminous coal and therefore low in volatile matter. No. 11 is also of fairly high rank (carbon, 87.4). Tar plus light oil rises fairly consistently with the gamma for low orders of the latter but as the gamma becomes fairly high there is a tendency toward deviation. Initial expansion and contraction temperature curves indicate no definite trends, but are included to show the contrast between them and similar curves for the bitumens, as the latter were fairly definitely correlatable with these functions.

A mild relationship is indicated between the gamma and the coke shatter, 900° C. on 3.81 cm., the trend of the latter being slightly upward on the average. The coke stability, 900° C. on 2.54 cm., however, shows little if any relationship.

CONCLUSION

The conclusion to be drawn from this intensive study of the relationship between solvent extraction or rational analysis data with other properties of coal is that one may interpret little from a knowledge of the quantities present of extractable constituents, with respect to significant differences in the restricted range of coking coals. Such few relationships as have seemed to be apparent from the charts shown are slight indeed and leave considerable room for doubt. For example, it would be unwise to predict with assurance any aspect of the behavior of coal during the coking process or any property of the coke produced, from the results thus far obtained.

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INDUSTRIAL USES OF COLOR CHARTS. Extensive use of various forms of charts as standards for color in specification of commodities is revealed by Bureau of Standards Letter Circular 358. The U. S. Army uses rectangles of silk as color standards for textiles, and colored paper cards as standards for paint, in the purchase of these materials. Colored cards are used by the Bureau of Aeronautics as standards for finishing material for aircraft. As a part of standardization of their products effected in coöperation with the Bureau of Standards, the school furniture industry adopted stained blocks of wood for color standards, and the sanitary ware industry adopted vitreous color standards. Extensive systems of color charts for general use have been published. The textile and allied industries have adopted "Standard and Seasonal Color Cards," in which silk is used for the standards. Despite the important part color plays in the paper industry, little effort has been made to standardize paper colors. It would seem that the use of standard color charts by the paper industry, rather than the present practice of matching samples submitted with orders, would lead to economy and the better satisfaction of all concerned.

Determination of Butadiene in Gases

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A method for the rapid, accurate, routine determination of butadiene in complex gas mixtures is described, in which molten maleic anhydride at 100° C. is used as the absorbent, the development of this method making possible the analysis of small samples of gas which heretofore could be analyzed only by very tedious and inaccurate methods.

THE method generally adopted for the estimation of the butadiene content of gases has consisted in the addition of bromine followed by the separation of the tetrabromide from admixed dibromides, derived from the olefins, by fractional distillation under reduced pressures and the calculation of the butadiene content of the original gas, as a maximum value from the crude tetrabromide or as a minimum value from either the recrystallized tetrabromide or the regenerated butadiene, the actual quantity being somewhere between these two figures (*5*).

Sorokin and Belikova (*8*) have determined butadiene by separating it as the tetrachloride.

The titrimetric method of Povarnin and Belikova (*7*) is based on the observation of Bergmann that the dibromide forms within 5 minutes, the tetrabromide after 12 hours.

Dobryanskii (*4*) has also proposed a titrimetric method based on the transformation of the butadiene into the tetrabromide by means of bromine liberated from a weighed quantity of potassium bromate. Markovich and Pigulevski (*5*) found this method to be unreliable for a number of types of gases, and good results were obtained only in the analysis of highly rectified butene-butadiene distillates.

A method similar to that of Dobryanskii, and with the modifications recommended by Davis, Crandall, and Higbee (*2*) to eliminate the disturbing influence of oxygen in these titrations, has been tried in this laboratory, but the results obtained by this method were inexact and quite unsatisfactory.

That quinones, azo esters, and various unsaturated aldehydes react with conjugated diolefins to form various ring compounds has long been known, and such reactions have recently been used in identifying the diolefins in various gasoline fractions.

Diels and Alder (*3*) record that the simple open-chain and cyclic butadienes unite with maleic anhydride to give anhydrocyclohexenes in quantitative yield, the butadiene addition product being *cis*-Δ^4-tetrahydrophthalic anhydride (m. p. 103–4° C.).

Most of these addition products are formed with the greatest ease, generally by allowing the diolefin and maleic anhydride to react in benzene solution at ordinary temperatures, the reaction involving the addition of one molecule of the diolefin to one of the maleic anhydride. The cyclic hydrocarbons react instantaneously with evolution of heat, but the addition with straight-chain diolefins is a slower process, butadiene, isoprene, and piperylene all reacting slowly in the cold, although readily at slightly elevated temperatures.

Birch and Scott (*1*) have made use of this reaction to isolate a number of diolefins from the fractions of a compression-plant gasoline from a high-temperature cracking unit.

Martin, Gruse, and Lowy (*6*) have studied the effect on gum formation of quantitatively removing conjugated diolefins from fractions of vapor-phase distillates by treatment with maleic anhydride.

The ready formation of these anhydrides having given an excellent method for the quantitative separation and identification of diolefins in liquid hydrocarbon mixtures, the purpose of this investigation was to apply the same reaction to the determination of butadiene in gases.

Preparation of 1,3-Butadiene

The butadiene used in these experiments was isolated from a cracked refinery gas. A quantity of the cracked gases, containing 3 to 5 per cent of butadiene, was passed through a small condensing trap cooled to −78° C. by solid carbon dioxide and acetone, a temperature at which all of the C-4 and a part of the C-3 hydrocarbons were condensed. These condensed hydrocarbons were then vaporized and passed through bromine in carbon tetrachloride at 0° C. The excess of bromine was removed and the carbon tetrachloride solution dried over calcium chloride. An equal volume of alcohol was added and the solution cooled in a solid carbon dioxide–acetone bath, whereupon almost the whole of the higher melting form of the butadiene tetrabromide crystallized out. For the regeneration of the butadiene, equal weights of the carefully purified tetrabromide (m. p. 118° C.) and zinc dust were placed in a flask with ethyl alcohol (approximately 2 cc. for each gram of the tetrabromide) at 0° C. and the whole allowed to warm slowly until the butadiene was liberated. Toward the end of the reaction, the flask was heated gently. The yield was almost quantitative and of high purity, as shown in the subsequent distillation on a low-temperature Podbielniak fractionating column as a means of further purification.

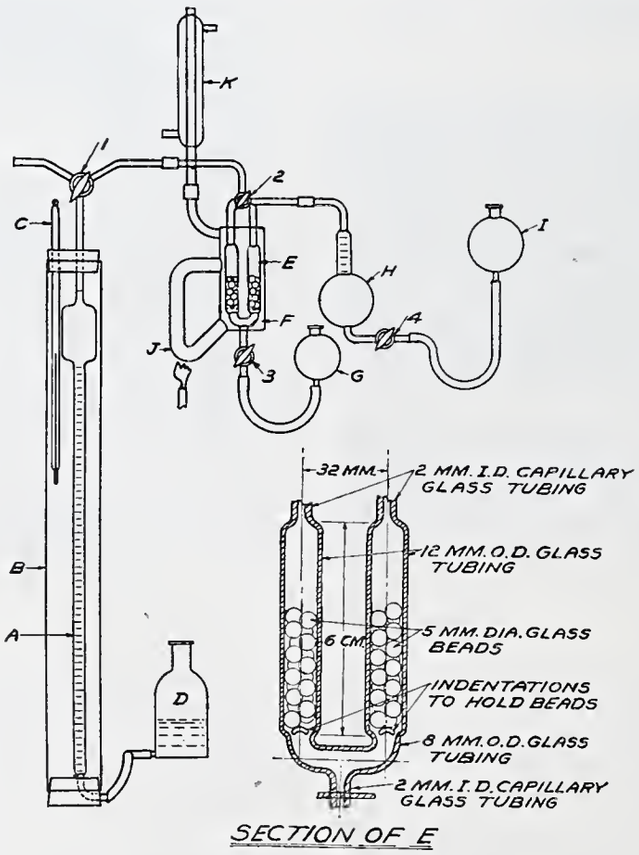

Figure 1. Diagram of Apparatus

Apparatus. Small amounts of molten maleic anhydride at 100° C. were found most suitable as an absorbent for

butadiene. The reaction between maleic anhydride and butadiene is rapid at 100° C., a decided advantage in using the molten anhydride. The gaseous hydrocarbons have an appreciable physical solubility in the molten anhydride, and in order to reduce this physical solubility to a minimum, small amounts of the anhydride must be used. Hence, it was necessary to design a special absorption pipet with which gas absorptions could be made with less than 2 cc. of absorbent, suitable means being provided for maintaining the temperature of the pipet at 100° C. These conditions have been very successfully met in the pipet shown in Figure 1. Pipets similar to the usual Orsat type, but heated by a steam jacket, requiring large amounts (125 grams) of maleic anhydride were not satisfactory, since the error caused by the physical solubility of the hydrocarbons could not be satisfactorily eliminated.

The apparatus, shown diagrammatically in Figure 1, consisted essentially of buret *A*, in connection with absorber *E*, through T-stopcock 2, and bulb *H* with the accompanying leveling bulb *I*. Leveling bulb *G*, containing mercury, permitted the displacement of the gas from the absorber. A small flame under *J* maintained a circulation of boiling water through jacket *F* and around absorber *E*, a few small glass beads in the lower bend of *J* promoting gentle boiling and a regular circulation. Buret *A* was surrounded by jacket *B* which contained water and thermometer *C*, reading to 0.1° C. Saturated salt solution, colored by the addition of a small amount of methyl red in sulfuric acid, was used in the buret, since it was found that maleic anhydride at 100° C. did not appreciably absorb water vapor from gases saturated with water vapor at ordinary temperatures.

Procedure. From 2.0 to 2.5 grams (1.5 to 2.0 cc.) of freshly distilled maleic anhydride were heated to approximately 100° C. in a shallow dish and drawn into the heated absorber *E* through stopcock 3. The rubber connection to *G* was then replaced and mercury introduced into *E* until all gas was displaced and the molten anhydride stood in the capillaries just above the top of jacket *F*. By means of mercury from *I*, all gas was displaced from *H* and the capillary connection to *E*.

A 50- to 100-cc. portion of the gas to be analyzed was taken into the buret, the mercury level in *E* lowered to the bottom of the U-tube, *E*, and the gas passed from *A*, through *E*, into bulb *H*, the rate of passage being regulated by adjusting stopcock 4. The gas was then passed back into *A*, through *E*, by lowering leveling bottle *D* and raising *I*. The gas remaining in *E* was displaced by raising the molten maleic anhydride into the capillaries just below stopcock 2. The volume was then read and the operation repeated once or twice until no further absorption was observed, the temperature of *E* being kept at 100° C. This preliminary passage of a portion of the gas was necessary in order to saturate the maleic anhydride with the hydrocarbons, or in case the maleic anhydride had been used in previous analyses, to bring the hydrocarbons already physically dissolved into equilibrium with those in the sample to be analyzed.

A sample of approximately 100 cc., measured to 0.1 cc., was then taken for the analysis and the absorption carried out as above, correction being made for any change in temperature.

Analysis of Synthetic Mixtures

Following the procedure outlined above, analyses were made of a number of synthetic mixtures containing known amounts of butadiene as a means of determining the accuracy of the method. The absorption of butadiene from a butadiene-nitrogen mixture containing 6.7 per cent of butadiene showed that the absorption was rapid and quantitative.

Table I. Analysis of Butadiene-Nitrogen Mixtures

Pass	Mixture I Volume	Mixture I Butadiene absorbed		Mixture II Volume	Mixture II Butadiene absorbed	
	Cc.	*Cc.*	%	*Cc.*	*Cc.*	%
	98.7	...	...	99.7	...	...
1	92.7	6.0	...	93.2	6.5	...
2	92.1	0.6	...	93.0	0.2	...
3	91.8	0.3	...	93.0	0.0	6.7
4	91.8	0.0	6.9	....	...	...

That the presence of isobutene had no influence on the absorption of butadiene was shown by absorptions from butadiene-isobutene-nitrogen mixtures containing approximately 10 per cent of isobutene.

Table II. Analysis of Butadiene-Isobutene-Nitrogen Mixtures

Components	Mixture I Calculated	Mixture I Found	Mixture II Calculated	Mixture II Found
Nitrogen	84.5	...	85.1	...
Isobutene	10.1	...	9.6	...
Butadiene	5.4	5.3	5.3	5.4

As a further check by means of synthetic mixtures, known amounts of butadiene were added to a cracked refinery gas and the resulting mixtures then analyzed. The small amount of butadiene present in the cracked gas was first removed by passage through maleic anhydride at 100° C. The cracked gas contained high percentages of ethylene, propene, and butene as well as appreciable amounts of the corresponding paraffins and pentane. The percentages of butadiene added to this gas are given in Table III, together with the values found by analysis for these mixtures.

Table III. Analysis of Cracked Gas–Butadiene Mixtures

Sample	Butadiene Calculated	Butadiene Found
	%	%
1	0.5	0.5
2	0.5	0.6
3	2.4	2.4
4	2.5	2.5
5	5.1	5.1
6	5.1	5.1
7	9.9	9.8
8	9.9	9.9
9	19.0	18.9
10	19.5	19.5

Acetylene (with air) in concentrations greater than 40 per cent was slowly but steadily absorbed. The volume absorbed per pass per 100 cc. of gas for concentrations to 100 per cent is shown in Table IV.

Table IV. Absorption of Acetylene by Maleic Anhydride at 100° C.

Acetylene	Volume Dissolved
%	*Cc./100 cc.*
30	0.0
40	0.0–0.05
50	0.1
100	0.5

Cracked gas–butadiene mixtures were then prepared containing 5 and 15 per cent of acetylene. The analysis of these mixtures, shown in Table V, indicated that acetylene in concentrations up to 15 per cent did not influence the accuracy of the butadiene determination.

Table V. Analysis of Cracked Gas–Acetylene–Butadiene Mixtures

Analysis	Acetylene	Butadiene Calculated	Butadiene Found
	%	%	%
1	5.0	14.9	14.9
2	15.0	5.0	4.9

The absorption of isoprene vapor (b. p. 35° C.) was found to be quantitative. Isoprene was vaporized in nitrogen to give a mixture containing approximately 10 per cent of isoprene vapor. This mixture was analyzed by absorption in 87 per cent sulfuric acid and by the maleic anhydride absorption. The data are shown in Table VI.

Table VI. Absorption of Isoprene Vapor by Maleic Anhydride

Analysis	Sample	Volume Per Cent of Isoprene Vapor By 87% H_2SO_4	By maleic anhydride	Calcd
1	1	13.1	11.6	...
2	1	13.1	11.6	...
3	1	..	11.7	...
4	2	..	1.2	1.3
5	3	..	1.5	1.4

The higher values obtained by the sulfuric acid absorption were undoubtedly due to the presence of olefins in the isoprene (from Eastman Kodak Company), most likely pentenes, since pentenes have been found in carefully fractionated isoprene obtained by the distillation of caoutchouc. That low values by the maleic anhydride absorption were not caused by an equilibrium between unreacted isoprene and the isoprene derivative *cis*-5-methyl-Δ^4-tetrahydrophthalic anhydride (m. p. 64° C.) is shown by the close agreement between the calculated and experimental values in analyses 4 and 5 on samples 2 and 3 which were obtained by diluting sample 1 with known volumes of air.

Comparison with Tetrabromide Method

The analysis of a cracked gas by the maleic anhydride method and by the tetrabromide method gave values in close agreement.

Table VII. Analysis of Cracked Gas by Maleic Anhydride and Tetrabromide Methods

Analysis	Method: Maleic anhydride	Method: Tetrabromide
1	3.5	3.8
2	3.4	3.8

The values by the tetrabromide method were 0.3 per cent high, as was to be expected, since this method is known necessarily to give somewhat higher than the correct values.

A sample of from 20 to 30 liters of gas and 3 or 4 hours' time are necessary for an analysis by the tetrabromide method, while the analysis can be made by the maleic anhydride method in 10 minutes and with samples of 100 cc. or less of gas.

Physical Solubility of Hydrocarbons

The gaseous hydrocarbons, other than butadiene, were found to have a very slight physical solubility in molten maleic anhydride at 100° C. However, the maleic anhydride was rapidly and completely saturated by passing a small portion of the gas once or twice through the anhydride. Using fresh maleic anhydride, the analyses in Table VIII were made successively on a cracked refinery gas.

Table VIII. Effect of Physical Solubility of Hydrocarbons on Analysis of Cracked Gas

Analysis	Butadiene in Cracked Gas	Butadiene in Cracked Gas Plus 50 Per Cent Air: Calculated	Butadiene in Cracked Gas Plus 50 Per Cent Air: Found
	%	%	%
1	3.6	...	...
2	2.6	...	...
3	2.5	...	...
4	2.5	...	...
5	...	1.3	1.0
6	...	1.3	1.3
7	...	1.3	1.3
8	...	1.3	1.4

In analysis 1 the value 3.6 per cent was too high, being caused by the physical solution of the hydrocarbons in the molten maleic anhydride. The values for analyses 2, 3, and 4, obtained after the saturation of the maleic anhydride by the paraffin and olefin hydrocarbons, are correct. The cracked gas contained a high percentage of hydrocarbons, so that more hydrocarbon was in physical solution than in the case of a gas containing a smaller percentage of hydrocarbons. This was shown in analyses 5 to 8 in which the hydrocarbon content was one-half of that in analyses 1 to 4. Analysis 5 gave a value 0.3 per cent low, caused by the release of a portion of the dissolved hydrocarbons on the passage of the gas containing a smaller percentage of hydrocarbon gases. The values for analyses 6, 7, and 8 were constant and indicated the correct butadiene content.

Hence, in the analysis of different types of gases, or of gases varying widely in content of hydrocarbons, it was necessary first to pass a portion of the gas through the maleic anhydride so as to saturate the reagent and establish equilibrium between the gas and the physically dissolved portion, thus eliminating errors which might otherwise arise from differences in the amounts of these hydrocarbons held in physical solution with various types of gases.

Analytical Absorbing Power of Molten Maleic Anhydride

The 2.0 to 2.5 grams of anhydride used in the pipet still actively absorbed butadiene after the absorption of 250 cc. However, crystals formed in the molten anhydride to such an extent after this amount had been absorbed that the anhydride was usually changed after absorbing approximately 150 cc. of butadiene. For the average sample, this would be over thirty analyses.

Application to Routine Analysis of Plant Gases

The method is now being used in this laboratory for the routine determination of butadiene in various plant gases. Typical analyses are shown in Table IX.

Table IX. Analysis of Plant Gases

Sample	Analysis 1	Analysis 2	Analysis 3
1	0.1	0.1	...
2	0.4	0.4	...
3	2.5	2.5	2.6

The method is proving to be of considerable value in determining the butadiene content of the gases from a number of pyrolysis experiments for which until now no method of determination has been available.

Summary

1. Molten maleic anhydride at 100° C. has been found a suitable reagent for the quantitative determination of butadiene in complex gas mixtures.

2. Olefins do not react with maleic anhydride and have no influence on the butadiene determination.

3. Acetylene in concentrations up to 15 per cent has no influence on the butadiene determination.

4. Errors which might be introduced by the physical solution of the hydrocarbons in the molten anhydride have been eliminated by using small amounts of the reagent and saturating it with the gas before the analysis.

5. Analyses made on synthetic mixtures containing known amounts of butadiene have shown the method to be very exact.

6. Approximately 10 minutes and 100 cc. or less of gas are required for an analysis.

7. The apparatus and procedure developed and described for this analysis are suitable for rapid, routine determinations.

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Analytical Reactions of Rubidium and Caesium

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A critical résumé is given of the known analytical methods for determining potassium, rubidium, and caesium. A reaction of rubidium and caesium is described that affords a satisfactory separation of these elements from potassium. A modification of the standard chloroplatinate procedure is suggested, and an improved method is proposed for the quantitative separation and determination of potassium, rubidium, and caesium, based on the use in succession of 9-phosphomolybdic, silicotungstic, and chloroplatinic acids.

The close similarity in the chemical behavior of potassium, rubidium, and caesium has led to numerous attempts to separate one from the other. In most instances the separations are only partial, and can be used for nothing more than a qualitative indication of the presence of two or all three of these alkalies. A few attempts have been satisfactory for the preparation of compounds of the pure individual rare alkalies, but none of the methods so far proposed is in any sense quantitative (*28*).

Among the reactions that have been used in alkali analysis are the standard perchlorate and cobaltinitrite methods, which precipitate all three alkalies without any separation. The same is true of the standard chloroplatinate method; Wernadski (*67*), however, claims a separation and determination of rubidium in a feldspar by fractional precipitation of the chloroplatinates. Brauner (*4*) says that 22 per cent of any lithium present is carried down as chloroplatinate with the potassium. Jenzsch (*33*) states that lithium and potassium form a mixed chloroplatinate. Smith and Shead (*56*) use lithium chloroplatinate as a precipitant for potassium. Robinson (*51*) removes most of the potassium from rubidium and caesium by fractional precipitation with chloroplatinic acid and strong hydrochloric acid. It is evident from these statements that the analyst should ascertain the composition of every final precipitate obtained from a mixture of alkalies in order to be sure of what he is weighing.

The alums have never had a wide use in quantitative alkali analysis because of their relatively high solubility, although, according to Browning and Spencer (*5*), they possess some advantages over the chloroplumbic and chloroantimonic acid methods.

Indirect analysis has long been employed (*8*, *12*, *27*) to determine potassium, rubidium, and caesium; using mixtures of standard solutions of these alkalies, however, the writers found that an error of 0.1 mg. in weighing the platinum from mixed chloroplatinates, or an error of 0.5 mg. in weighing silver chloride from the mixed chloroplatinates, was multiplied by subsequent calculations as much as seventy fold, giving positive and negative deviations as high as 30 per cent from the true values. Bunsen (*8*) urges caution in accepting the results obtained by indirect methods.

Potassium, rubidium, and caesium phosphotungstate (*38*, *46*) are the most insoluble salts known of these alkalies but, as in the case of the above-mentioned reactions, no separation is effected.

Sodium silicomolybdate (*31*, *32*, *38*, *45*) is at present used to separate rubidium and caesium from potassium; it is, however, by no means quantitative for caesium, much less for rubidium, but serves for technical purposes.

Silicotungstic acid (*16*, *22*, *37*) is a quantitative precipitant for caesium and does not ordinarily precipitate potassium or rubidium (*19*); under conditions described in detail below, this reagent affords a satisfactory separation of caesium from potassium and rubidium.

Germanotungstic acid (*6*, *54*) was found to be less sensitive toward rubidium and caesium than the corresponding silico complex, but can be used for the qualitative detection of these alkalies in the presence of potassium. Attempts to form insoluble titanotungstates (*36*) failed.

The fluosilicates of potassium (*52*) and rubidium (*7*) are too soluble for a quantitative separation from the corresponding caesium (*48*) salt; no solubility data were available for the fluotitanates (*47*) and fluotantalates, but investigation showed that they behaved like the fluosilicates. Potassium is the least soluble of the fluogermanates (*40*, *68*) and is too soluble for quantitative work.

Caesium and rubidium chlorostannate (*9*, *28*, *39*, *55*, *59*, *60*) are the compounds most often used in rare alkali analysis; they are not, however, quantitative except under conditions that cause an appreciable co-precipitation of the potassium compound. Caesium bromostannate (*38*, *49*) is much more insoluble than the chlorostannate, and the corresponding potassium salt is hard to prepare; on the other hand, rubidium bromostannate is considerably more soluble than the chloro compound; bromostannic acid consequently shows some specificity toward caesium, but not sufficient to warrant its use in accurate work. The iodostannates (*1*) of rubidium and caesium are employed in microscopic qualitative analysis, but the authors found them much more soluble than the chlorostannates, which makes them well suited for microscopic analysis (*11*).

The chloroplumbates (*65*) have been discarded even for qualitative work; they are the least soluble of the lead halide complex salts.

Reed and Withrow (*50*) claim that potassium alone precipitates as a double zirconium sulfate, while rubidium and caesium do not; on the other hand, Yajnik and Tandon (*70*) say that all three alkalies are quantitatively precipitated as zirconium sulfate.

Sodium bismuth thiosulfate (*10*, *30*) precipitates all three of the alkalies.

It was found that rubidium and caesium bismuthinitrites (*2*) would precipitate only when moderately concentrated, and that the filtrates from such precipitations always yielded a positive reaction with chloroplatinic acid; although the bismuthinitrites afford a separation of rubidium and caesium from potassium, they are too soluble for quantitative work.

Caesium bismuth iodide (*66*) is sufficiently insoluble to recommend its use in microscopic analysis as a specific reagent for caesium, but has never found a place in quantitative procedures; Tananaeff (*62*, *63*), however, states that he effects a quantitative separation of caesium from rubidium by means of this reagent.

Godeffroy (*21*) lists a number of rubidium and caesium salts whose low solubilities make them useful for fractional crystallization; they are not, however, quantitatively insoluble, and most of them exhibit some specificity toward caesium. Of these the best known is the double caesium and antimony chloride (*20*); the somewhat more insoluble caesium antimony iron chloride (*60*) is a later modification of Godeffroy's work. The antimony chlorides are more used at present as specific reagents for caesium than any other, but are not quantitative (*39*) except under conditions that cause appreciable co-precipitation of rubidium.

Murmann (*42*) reports some very insoluble complex ferrocyanides of caesium, rubidium, and potassium with calcium and magnesium; they are of doubtful composition, they require an excess of alkali to effect precipitation, and their complexity makes them difficult to work with after they have been obtained.

Potassium and rubidium picrates, bitartrates, and especially their chloronitrotoluenemetasulfonates (*13*) are useful for a qualitative separation of these elements from caesium. The last of the three forms the most insoluble compounds, but in the authors' hands no precipitate could be obtained from solutions containing as much as 10 mg. of rubidium chloride per cubic centimeter; it was found that potassium was more sensitive to the reagent than rubidium, although Noyes and Bray (*43*) state that 0.5 mg. of rubidium gives an almost immediate precipitate with this reagent. In the hope that there might be some deviation from the rule of increasing solubility with increasing atomic weight, the bromo derivative of this reagent was prepared and tried; it was still less sensitive, however, toward potassium and rubidium than the chloro compound.

The literature contains numerous references to microscopic tests (*3,17,25,26,64*) for the alkalies; these tests usually require rather high concentrations of the elements in question, and claim little or no chemical specificity for potassium, rubidium, or caesium, and consequently have no use in quantitative analysis.

Visual spectroscopic (*23, 24*) methods of estimation have not yet been sufficiently developed to warrant their use in accurate work; spectrographic methods are at present still less serviceable because of the effects of "pulsion."[1] The lower limit of spectrographic sensitivity for salts of potassium, rubidium, and caesium is reached when these salts are reduced to 1 per cent of the diluting medium; using the arc-flame method, the limit is in the neighborhood of 0.1 per cent of the diluting medium.[2] When, however, potassium, rubidium, or caesium is present in a silicate rock, presumably as a refractory aluminosilicate, each is very much more sensitive still.

Having noticed that reagents for alkalies were used also as precipitants for alkaloids, the writers tried on the alkalies the effect of a number of compounds that are usually used in alkaloid analysis. Picrolonic acid, xylic acid, *o*-toluic acid, phenylacetic acid, and phenylpropionic acid gave no precipitates with potassium, rubidium, or caesium. Neither was there any precipitation with phosphoantimonic acid (*53*). It is known that the potassium (*34*), rubidium (*14*), and caesium salts of 12-phosphomolybdic acid are quantitatively insoluble; so also are the potassium (*61*), rubidium (*15, 18*), and caesium salts of 10-phosphomolybdic acid.

New Reaction of Rubidium and Caesium

As luteophosphomolybdic (9-phosphomolybdic) acid (*34*) was known to precipitate a number of alkaloids quantitatively, without precipitating potassium, and as there was no mention in the literature of its effect on rubidium and caesium, the writers investigated and found that this reagent precipitated both rubidium and caesium quantitatively in the presence of potassium. These unrecorded reactions were then made the basis of a method for the quantitative separation and determination of potassium, rubidium, and caesium.

Kehrmann and Böhm (*34*) prepared 9-phosphomolybdic acid by adding a slight excess of phosphoric acid to the dodeca acid and allowing it to stand for several months; on standing, the dodeca acid gradually lost its power to precipitate potassium, and changed into the luteo acid. Decaphosphomolybdic acid behaves in the same way in the presence of phosphoric acid.

Kehrmann and Böhm (*34*) state that the potassium salt of 9-phosphomolybdic acid is about of the same order of solubility as potassium sulfate, and can easily be salted out; consequently too concentrated a solution of potassium salt must not be used in testing for the completion of the reaction. Once precipitated, potassium 9-phosphomolybdate is dissolved again with difficulty.

It has been found best, however, to prepare the luteo acid by heating the commercial dodeca acid carefully to between 300° and 350° C. with continuous stirring so as to avoid local overheating; at this temperature the dry acid turns from orange to green. The temperature is maintained until no orange particles remain; the acid is then cooled and extracted with water. The green solution is oxidized with a little bromine water, and on slow evaporation the short, stout, yellow prisms of the luteo acid separate out. This procedure eliminates an excess of free phosphoric acid in the reagent, the presence of which tends to retard precipitation (*58*) of the alkali phosphomolybdates.

Ephraim and Herschfinkel (*18*) report a rubidium salt of 9-phosphomolybdic acid, $Rb_6PO_4.9MoO_3$, which does not correspond in composition with the potassium salt $K_3PO_4.9MoO_3.7H_2O$ obtained by Kehrmann and Böhm (*34*). Several attempts made by the writers to determine the formula of the caesium salt showed that it approximated more closely the composition of the potassium salt, but the analyses were not satisfactory; duplicate analyses of a salt prepared by precipitating caesium with an excess of luteo acid, while consistent in themselves, did not agree with the results obtained when the salt was precipitated in the presence of an excess of caesium. In both cases the summation was low if the molybdenum was calculated to MoO_3, and high if calculated to Mo_2O_7. For these reasons, no attempt has been made to analyze the rubidium salt. The results obtained with the caesium salt are listed in Table I; the molybdenum was precipitated as sulfide from a sodium sulfide solution, was reprecipitated as lead molybdate, weighed, and calculated to the oxide; caesium was precipitated from the filtrate as chloroplatinate; the excess chloroplatinic acid was then reduced with zinc, and the phosphorus was separated and weighed as zinc pyrophosphate.

In the salt precipitated in the presence of excess luteo acid, the ratio of the components is as follows:

$$P : Mo = 1 : 9.1; \quad P : Cs = 1 : 1.7; \quad \text{and } P : H_2O = 1 : 6.4$$

The ratios in the salt precipitated in the presence of excess caesium ion are:

$$P : Mo = 1 : 8.8; \quad P : Cs = 1 : 2.19; \quad \text{and } P : H_2O = 1 : 5.4$$

The precipitates are so finely divided that their optical properties give no indication whatever as to whether the material is homogeneous or a mixture.

In order to determine the quantitativity of 9-phosphomolybdic acid as a precipitant for rubidium and caesium, a number of determinations were made on mixtures of known solutions of these salts, each of which had previously been

[1] The term "pulsion" has been coined to designate the variation in intensity of spectral lines as conditioned by ionization phenomena (*35, 44*). Work on this subject will be published shortly.

[2] An article on the arc-flame method will be published in the near future.

analyzed separately by the chloroplatinate method. For the reasons given above, the precipitates were not weighed directly as such; the molybdenum was first removed with hydrogen sulfide, and the alkali was recovered from the filtrate and weighed as chloroplatinate. The results of these determinations are listed in Tables II and III.

Table I. Analysis of Caesium Salt of 9-Phosphomolybdic Acid

	MoO_3	Cs	PO_4	H_2O
	Gram	*Gram*	*Gram*	*Gram*
Salt precipitated in presence of excess luteo acid. Found in 0.5000-gram sample	0.3673	0.0632	0.0263	0.0320
Salt precipitated in presence of excess caesium ion. Found in 0.5000-gram sample	0.3518	0.0804	0.0262	0.0271
Theoretical for $Cs_3PO_4.9MoO_3.7H_2O$	0.3383	0.1040	0.0248	0.0328
Theoretical for $Cs_3PO_4.9MoO_3$	0.3621	0.1113	0.0265	..

Table II. Separation of Rubidium from Potassium by 9-Phosphomolybdic and Chloroplatinic Acids

Taken		Obtained		Recovery
KNO_3	RbCl	Rb_2PtCl_6	RbCl	
Gram	*Gram*	*Gram*	*Gram*	%
1.00	0.0339	0.0798	0.0335	98.8
1.00	0.0339	0.0812	0.0341	100.6
1.00	0.0226	0.0540	0.0225	99.5

Table III. Separation of Caesium from Potassium by 9-Phosphomolybdic and Chloroplatinic Acids

Taken		Obtained		Recovery
KNO_3	CsCl	Cs_2PtCl_6	CsCl	
Gram	*Gram*	*Gram*	*Gram*	%
1.00	0.0205	0.0406	0.0203	99.0
1.00	0.0192	0.0380	0.0190	98.9
1.00	0.0095	0.0192	0.0096	101.0

The final precipitates were examined spectroscopically by the arc-flame method to determine what was being weighed, and in most cases a small amount of potassium was detected. A number of the experiments were repeated, adding the reagent first to potassium alone; when no precipitation had occurred after a long interval, either rubidium or caesium was added, causing immediate precipitation. The continued presence, however, of lines due to potassium in the spectrograms suggests that the potassium was probably adsorbed by the rubidium and caesium phosphomolybdates. Spectrographic examination of the filtrates from the phosphomolybdic acid treatment showed that the rubidium and caesium had been removed.

Separation of Caesium from Rubidium

Having quantitatively removed potassium, the next step was to separate rubidium and caesium from each other. The reagent used for this purpose was silicotungstic acid. Freundler and Ménager (*19*) found that rubidium silicotungstate is soluble to such an extent that 0.4 gram of rubidium per 100 cc. of solution is not recoverable. The writers found that caesium silicotungstate is quantitatively precipitated, in the presence of rubidium, in 6 *N* hydrochloric acid, and that the rubidium is quantitatively recoverable from the filtrate as chloroplatinate. The precipitation of caesium is much more rapid in 8 *N* sulfuric acid, but the separation from rubidium is not as sharp as when hydrochloric is used; nitric acid tends to prevent precipitation of both rubidium and caesium silicotungstate. The caesium precipitate is somewhat hygroscopic, and there is a tendency for silicotungstate precipitates to form several hydrates (*69*), so the caesium was also converted (*22*) to chloroplatinate for weighing. Tables IV and V show the quantities of rubidium and caesium recovered separately from their silicotungstates, and Table VI shows the results of the silicotungstic acid separation of rubidium from caesium.

The amount of rubidium that can be separated from caesium is governed by the solubility of the former as silicotungstate; the writers have found it advisable to use not more than 0.08 gram of rubidium chloride in a volume of 50 cc. of 6 *N* hydrochloric acid, and to use an excess of not more than 0.2 or 0.3 gram of solid silicotungstic acid over the amount required to effect precipitation of the caesium; otherwise the separation may not be satisfactory. The amounts of potassium, rubidium, and caesium used in the preliminary experiments were chosen primarily from consideration of the actual quantities that will confront the analyst in silicate mineral work. At these concentrations, the caesium recovered is spectroscopically free from potassium, but usually contains a trace of rubidium; on the other hand, the rubidium is entirely free from caesium; if potassium was present in the original mixture, spectroscopic examination may show that a small quantity of the potassium has been carried down with the rubidium chloroplatinate.

Table IV. Recovery of Rubidium from Silicotungstic Acid by Chloroplatinic Acid

Taken	Obtained		Recovery
RbCl	Rb_2PtCl_6	RbCl	
Gram	*Gram*	*Gram*	%
0.0226	0.0532	0.0222	98.2
0.0188	0.0450	0.0187	99.4
0.0226	0.0539	0.0225	99.5
0.0342	0.0812	0.0341	99.7

Table V. Separation of Caesium from Potassium by Silicotungstic and Chloroplatinic Acids

Taken		Obtained		Recovery
KNO_3	CsCl	Cs_2PtCl_6	CsCl	
Gram	*Gram*	*Gram*	*Gram*	%
0.20	0.0175	0.0350	0.0175	100.0
0.20	0.0175	0.0350	0.0175	100.0
0.20	0.0102	0.0198	0.0099	97.0
1.00	0.0095	0.0190	0.0095	100.0

Table VI. Separation of Caesium from Rubidium by Silicotungstic and Chloroplatinic Acids

Mixture Taken		Obtained				Recovery	
RbCl	CsCl	Rb_2PtCl_6	RbCl	Cs_2PtCl_6	CsCl	RbCl	CsCl
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	%	%
0.0226	0.0095	0.0532	0.0222	0.0193	0.0095	98.2	100.0
0.0342	0.0095	0.0816	0.0341	0.0196	0.0096	99.7	101.0
0.0226	0.0189	0.0540	0.0225	0.0370	0.0185	99.5	97.9

The filtrate from the 9-phosphomolybdic acid precipitation contains all the potassium, except as noted above, which can be determined by any of the three standard methods mentioned above.

Table VII shows the recoveries of rubidium and caesium from known mixtures containing aluminum, potassium, rubidium, and caesium nitrates, by means of 9-phosphomolybdic and silicotungstic acids.

Modifications of Chloroplatinate Method

During long use of the chloroplatinate method the writers have developed several minor modifications thereof that secure more concordant results and greater flexibility of application, without necessity for the usual meticulous precautions.

Table VII. Separation of Rubidium and Caesium from Potassium and from Each Other by 9-Phosphomolybdic, Silicotungstic, and Chloroplatinic Acids, in Presence of Aluminum Nitrate

Mixture Taken				Obtained				Recovery	
KNO_3	$Al(NO_3)_3$	RbCl	CsCl	Rb_2PtCl_6	RbCl	Cs_2PtCl_6	CsCl	RbCl	CsCl
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	%	%
1.00	0.50	0.0339	0.0195	0.0818	0.0342	0.0402	0.0201	100.8	103.0
1.00	1.00	0.0226	0.0095	0.0540	0.0225	0.0185	0.0093	99.5	98.0
0.80	1.00	0.0226	0.0095	0.0536	0.0224	0.0196	0.0098	99.1	103.1

1. The nitrates of the elements are much more soluble in ethyl alcohol than the chlorides. Standard texts on analytical chemistry premise that alkali chlorides must be used in the chloroplatinate method, and consequently the alkalies must first be assembled and removed from all other salts before proceeding with the analysis. It has been found, however, that potassium, rubidium, and caesium chloroplatinates can be precipitated quantitatively without contamination, in alcohol, in the presence of large amounts of sodium, iron, aluminum, manganese, and other salts, provided everything in the solution has previously been converted to nitrate.

2. It has been found more satisfactory to precipitate the alkali chloroplatinates instead of converting to chloroplatinate by evaporation everything that is present and leaching out the soluble salts. Precipitation is effected quantitatively and immediately by adding chloroplatinic acid to the solution containing 60 to 70 per cent of alcohol by volume, and then adding 2 or 3 cc. of ethyl ether. Direct precipitation of the alkalies has the obvious advantages of rapidity and of eliminating the possibility of positive or negative error through occlusion or decrepitation; furthermore, direct precipitation obviates such objectionable contaminants of the reagent as nitroso- and hydroxychloroplatinic acids (*29*).

Rubidium and caesium are listed as chlorides in the tables in this paper only for convenience in comparing amounts of standard solutions taken with amounts recovered as double platinum chloride; as will be seen, the chlorides were actually converted to nitrates in all the analyses.

Improved Analytical Method for Potassium, Rubidium, and Caesium

The following method is therefore proposed for determining rubidium and caesium in the presence of potassium:

A sample is taken that contains not more than 0.08 gram of rubidium chloride and not more than about 1.0 gram of potassium chloride. The sample is dissolved in 100 cc. of nitric acid (1 to 3), heated almost to boiling, and treated with 9-phosphomolybdic acid until precipitation is complete, observing the usual precautions of the similar standard method for the precipitation of ammonium phosphomolybdate. When the yellow precipitate of rubidium and caesium 9-phosphomolybdate has settled, it is filtered through a Munroe (*41, 57*) crucible, and washed with 1 per cent sodium nitrate solution. The filtrate now contains all the potassium, which can be determined by any of the first three methods mentioned.

The phosphomolybdate precipitate is then dissolved in the least necessary amount of dilute sodium hydroxide solution; the resulting solution is saturated with hydrogen sulfide, heated to boiling, and made just acid with nitric acid; this usually serves to precipitate all the molybdenum as sulfide. The solution is then boiled to coagulate the precipitate, which is filtered off, washed, and discarded. It is essential that the molybdenum be removed from the rubidium and caesium, otherwise their very insoluble phosphomolybdates will reprecipitate and interfere with the separation of one from the other; the sulfide method has been found to be the most satisfactory for this purpose. If some molybdenum is reduced and left unprecipitated, it can readily be oxidized by boiling with a little bromine water, and after cooling can be treated again with hydrogen sulfide.

Caesium can be separated from rubidium in the filtrate by the silicotungstic acid method described below, but because of the phosphates present it has been found more satisfactory first to concentrate these alkalies as chloroplatinates.

The filtrate from the removal of molybdenum is evaporated to about 20 cc., and after adding 60 cc. of 95 per cent alcohol, is treated with a slight excess of chloroplatinic acid, and then a few cubic centimeters of ether are added; after the precipitate has settled it is filtered through a Munroe crucible. Besides rubidium and caesium, the precipitate always contains a little sodium phosphate; consequently it cannot be weighed at this stage. After washing with 80 per cent alcohol, a fresh receiver is placed under the crucible, and to the latter are added a little distilled water and 2 or 3 drops of hydrazine hydrate; the reaction is then allowed to proceed till vigorous evolution of gas ceases. Complete reduction of the chloroplatinates takes place immediately, with the formation of platinum and of the chlorides of the alkalies. Suction is then applied, and the alkali chlorides are washed into the flask.

The excess hydrazine must now be removed from the alkalies, because it forms very insoluble compounds with both silicotungstic and chloroplatinic acids. It is most conveniently removed by boiling for a short time with a little aqua regia, which should be added cautiously; otherwise the reaction may be violent.

The solution is now evaporated to small volume with some concentrated hydrochloric acid to insure complete removal of nitric acid, it is taken up in 50 to 75 cc. of 6 *N* hydrochloric acid, and to the cold solution is added 0.5 to 1.0 gram of solid silicotungstic acid dissolved in a few cubic centimeters of water. (The reagent supplied by Eimer and Amend has been found very satisfactory.) Precipitation will be incomplete if nitric acid has not been entirely removed. After standing for 12 hours, the precipitated caesium salt is filtered through a Munroe crucible, and is washed with 6 *N* hydrochloric acid. The filtrate contains all the rubidium, which is determined as chloroplatinate by evaporating to 10 cc. in the presence of nitric acid and a little chloroplatinic acid, adding 3 times its volume of alcohol together with a small excess of chloroplatinic acid and a little ether, filtering, washing with alcohol, drying, and weighing in the usual way. The excess silicotungstic acid does not interfere with the determination, provided there is a little chloroplatinic present to prevent precipitation of the rubidium as silicotungstate during the process of evaporation.

It is preferable, as has been already stated, to weigh the caesium as chloroplatinate. To do this, the silicotungstate radical must be removed, and best results are obtained by the following procedure (*22*):

The caesium precipitate is dissolved by the least excess of sodium hydroxide; this solution is made faintly acid with nitric acid, is diluted to 200 cc., and to it in the cold is added 10 per cent mercurous nitrate solution till precipitation is complete; at this point, the mercurous silicotungstate flocculates and settles rapidly. The precipitate is filtered off, washed with 1 per cent mercurous nitrate solution, and discarded. If an electrolyte is not present in the wash water, the mercurous silicotungstate will be peptized and will pass through the filter paper. Then the excess mercurous salt in the filtrate is oxidized with a little aqua regia to the mercuric state, when it is quite soluble in alcohol; the solution is evaporated to 10 cc. as for the determination of rubidium, treated with three times this volume of alcohol, then with chloroplatinic acid and with ether, and the caesium is filtered off and weighed as chloroplatinate.

The method proposed does not afford the clean-cut sharpness of separation that is desirable in an accurate quantitative procedure; on the other hand, it compares favorably with a number of other standard methods in current use for the determination of elements that are chemically not so closely allied as are the rare alkalies, such as silicon, germanium, tin, and arsenic; this method is furthermore much more reliable than those hitherto proposed. The average error introduced in the course of analysis by this method is ±2 per cent, which could conceivably be reduced by the use of larger amounts of material. No effort has been made to use larger amounts because, on account of the rarity of rubidium and caesium, the quantities dealt with in this paper represent what the analyst will ordinarily encounter. The method is now being applied in the analysis of some rubidium- and caesium-bearing minerals.

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Retention of Dichromate by Glassware

After Exposure to Potassium Dichromate Cleaning Solution

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It has perhaps not been generally realized that the use of cleaning solution ($H_2SO_4 \cdot K_2Cr_2O_7$ mixtures) may be a source of trouble in biology, chiefly through contamination of media kept in contact with glassware cleaned by this method. Some workers, suspicious of cleaning solution, have regarded the ordinary rinsing with tap water and distilled water as inadequate, and have resorted to longer periods of washing, the assumption apparently being, that whereas rinsing removed the cleaning solution on the surface of the glass, it did not extract that which had penetrated into the glass. As far as can be gathered from the literature, no systematic biological or chemical assay has ever been attempted to determine the adequacy of rinsing and washing procedures in ridding glassware of cleaning solution.

α, δ-Diphenylcarbohydrazide $(C_6H_5NHNH)_2CO$ has been known for a long time. In 1900 Cazeneuve (*2*) suggested it as an extremely sensitive reagent for detecting potassium chromate. It was subsequently used by Barnebey and Wilson (*1*) as an indicator for the dichromate titration of iron.

Chromate or dichromate oxidizes α, δ-diphenylcarbohydrazide to diphenylcarbazone ($NH_2NHCON{:}NH$), a reaction which gives a well-defined pink coloration to the solution and is so delicate that 0.0001 mg. (0.1γ) can be easily detected. Moreover, in somewhat greater concentration, the color value is adaptable for a colorimetric determination.

Procedure

α,δ-Diphenylcarbohydrazide was prepared by dissolving 0.5 gram of the dry powder in 70 ml. of 95 per cent alcohol and 25 ml. of glacial acetic acid and making the solution up to 100 ml. with distilled water in a volumetric flask. The reagent keeps about 3 hours at room temperature, after which a pink color develops, presumably due to an oxidation similar to that effected by the chromate.

The standards were prepared so as to contain respectively 5.0, 4.0, 3.0, 2.0, 1.0, 0.5γ of potassium dichromate per 5 ml. To each of these tubes 1 ml. of the α,δ-diphenylcarbohydrazide reagent was added. It required about 10 minutes at room temperature for the full pink color to develop. After about 45 minutes the color gradually began to fade, so that it was necessary to make all comparisons at least within 0.5 hour after the standards and unknowns had been prepared. For the comparison a Klett colorimeter was used with 5-ml. cups. Concentrations below 0.5γ were not adaptable for measurement in the colorimeter because of low color value, but were simply roughly estimated. In general, anything less than 0.2γ was considered a trace.

It was assumed that ten rinsings with water, seven of tap and three of distilled, constituted adequate removal of all potassium dichromate from the surface of the glass. This was borne out by tests. However, any potassium dichromate which had in some manner been retained within the glass might not be so quickly removed by rinsing. Hence all the tests reported were done on wash waters which had been in contact with the glass for various lengths of time. These extractions with water were sometimes repeated twice in

order to gain some idea of the rate of diffusion of potassium dichromate out of the glass. In spite of the delicacy of the reaction, it was found necessary to concentrate all wash waters by heat evaporation before applying the test. This was always done in a container other than the one used in the test. In one series of tests, the wash water was kept hot during the extraction period in order to see whether hot water would effect a more speedy removal of the retained potassium dichromate than cold water.

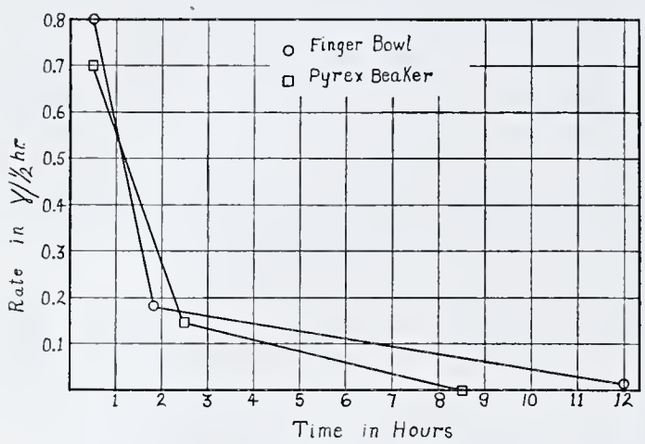

Figure 1. Rate of Diffusion of Dichromate from Glassware Exposed to Cleaning Solution

Glassware for the tests was taken at random from the shelves of the Chemical Room, no attempt being made to trace its history. The tests were concentrated, however, on two types of glass: Pyrex, consisting of beakers, flasks, test tubes, and other miscellaneous pieces; and lime glass, consisting mostly of finger bowls, which are so largely used in the Marine Biological Laboratory. The largest amounts of dichromate recovered from glass were of the order of 5γ or 0.005 mg., a concentration of 5 parts per million in a 1-gram sample. Such concentrations, while of no importance in the ordinary chemical procedures, are presumably significant when the glass is used for storage of biological specimens.

Results

Table I presents experiments done on miscellaneous glassware selected at random, exposed to cleaning solution and wash water for varied lengths of time. Examination of the data reveals that short or long exposure to cleaning solution (within the limits of 6 to 18 hours) does not seem to influence the amount of potassium dichromate recovered from the wash waters. Thus, in the case of experiments 1 and 2, it might be expected that the glass exposed longer should retain the larger amount of potassium dichromate, the extraction periods being roughly equal, but the reverse is true. However, since none of the glassware was new and its history was unknown, differences might occur in the nature of the glass surface exposed which would influence the rate of penetration of potassium dichromate. Furthermore, there is reason for believing that the rate of penetration of potassium dichromate into the glass is initially large but decreases rapidly with time, so that glass exposed 10 hours might not contain much more potassium dichromate than glass exposed 1 hour. Referring to Table II, it can be seen that the use of hot water is very effective in increasing the rate of removal of dichromate from glass. Thus, during the first half-hour extraction period, the hot water removed 0.7γ and cold water only 0.2γ. Additional proof of this action is seen in the second and longer extraction period. Here comparison of the wash waters (both cold) shows that the glass initially extracted hot gave blank tests, while that extracted cold continued to show traces of dichromate.

Table I. Recovery of Potassium Dichromate in Wash Water

(Miscellaneous glassware)

Experiment	Glassware	Contact with Cleaning Solution	Contact with Wash Water	Volume of Wash Water	$K_2Cr_2O_7$ Recovered
		Hours	*Hours*	*Ml.*	γ
1	Small finger bowl, lime glass	17.5	12.5	140	1.8
2	Small finger bowl, lime glass	6	16.33	145	5.3
3	50-ml. flask, Pyrex	6	16.5	50	0.8
4	Test tube, Pyrex	6.25	15.75	20	Trace
5	Test tube, lime glass	6.75	15.75	20	Trace
6	100-ml. beaker, Pyrex	5.75	0.75	95	2.0
7	50-ml. beaker, Pyrex	17	0.5	45	1.6
8	50-ml. beaker, Pyrex	17	0.5	45	1.2
9	Black glass depression block, lime glass	6.5	16.5	75	0.6
10	Clear glass depression block, lime glass	6.5	16.5	75	0.7
11	Large beaker, Pyrex	One month	3.25	85	5.0

Table II. Recovery of Potassium Dichromate from Glassware by Hot and Cold Wash Water

(Pyrex beakers, 250 ml. capacity, exposed to cleaning solution for 15 hours)

Experiment	$K_2Cr_2O_7$[a] Recovered	$K_2Cr_2O_7$[b] Recovered
	γ	γ
	Cold water	Cold water
1	0.2	Trace
2	0.2	Faint trace
3	0.2	Trace
	Hot water	Cold water
4	0.7	Blank
5	0.7	Blank
6	0.7	Blank

[a] 30-min. contact with wash water.
[b] 2-hour contact with wash water.

Table III presents data obtained from a series of finger bowls and Pyrex beakers of nearly the same capacity. It is seen from Tables I and III that there is no well-defined difference between Pyrex and lime glass in regard to retention of potassium dichromate. The point to be particularly stressed is that, without exception, the rate of diffusion of potassium dichromate out of the glass and into wash water is not a linear function of time. This is clearly shown in Figure 1. An extremely rapid initial rate of diffusion of potassium dichromate out of the glass results in approximately 50 per cent removal in the first 30 minutes and 80 per cent in 2 hours. Even prolonged third extractions with wash water may contain traces of dichromate, indicating that residual amounts of dichromate leave the glass extremely slowly.

Table III. Recovery of Potassium Dichromate from Glassware by Wash Water during Successive Periods of Extraction

Experiment	Contact with Cleaning Soln.	Period 1 Contact with wash water	Period 1 $K_2Cr_2O_7$ recovered	Period 2 Contact with wash water	Period 2 $K_2Cr_2O_7$ recovered	Period 3 Contact with wash water	Period 3 $K_2Cr_2O_7$ recovered
	Hrs.	*Hrs.*	γ	*Hrs.*	γ	*Hrs.*	γ
	FOUR-INCH LIME-GLASS FINGER BOWLS, 270 ML. CAPACITY						
1	3.5	0.5	0.8	1.33	0.5	11	0.3
2	3.5	1.66	0.2	11	0.3	..	...
3	3	0.5	0.8	1.33	Trace	11	Trace
4	3	1.66	0.75	11	Trace	..	...
5	35	0.5	1.4	1	Trace	11	Trace
6	35	1.5	5.5	11	Trace	..	...
	PYREX BEAKERS, 250 ML. CAPACITY						
1	1	0.5	0.7	2	0.6	6	Blank
2	4	0.5	0.75	2	0.25	6	Blank
3	4	2	0.9	...	..	..	...
4	8	0.5	0.5	2	Blank	6	Blank
5	8	2	0.6	...	..	..	...

The safest and quickest method of disposing of the dichromate retained in the glass seems, therefore, to boil it out with several successive changes of boiling water, allowing at least 15 minutes for each treatment. Running cold water can also be used, but would probably require much longer.

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Comparison of Wet- and Dry-Film Hiding-Power Tests

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Hiding power of paint or pigment is shown to be a function of concentration of the pigment in the film. A comparison of wet- and dry-film tests shows the two types to yield significantly different relations between hiding power and pigment concentration, which are shown to be, in part, due to actual differences in concentration of pigment in wet and dry films of the same paint. The author concludes that it is unsafe, in general, to employ a wet-film test.

A new dry-film test is described which gives hiding powers paralleling those obtained at either 2 per cent contrast or complete hiding in the dry film. The test is easily carried out, has good reproducibility, and may be used for comparisons at any contrasts or film thicknesses to beyond practical complete hiding to show relative values of paints or pigments.

THE hiding power of a paint may be determined in a number of ways (*1–5, 7*). Tests employing either wet or dry films are in common use, and definite advantages and disadvantages are attributable to each.

Wet-film tests have been favored as most easily adaptable to securing results at so-called complete hiding. Results are obtained as absolute values, and use of the wet paint permits speed and fair reproducibility in testing. As commonly carried out, however, the application of the results to the practical use of the paint is questionable. Paint is applied at several times the normal one-coat thickness over backgrounds of rigorous and extreme contrast, until these backgrounds are visually completely obliterated under the most exacting conditions of observation. Perhaps the most serious objection is that the wet paint film in test is chemically and physically quite different from the dry film which actually represents the paint in use.

Results at complete hiding can also be obtained with the dry film, but methods which have been available have been so difficult and time-consuming as to secure little recognition. Paints are more commonly compared at one or two normal coats over a contrast background for purely relative values. The advantage of this type of test is that differences between paints may be made directly visible. The test is carried out under conditions much more nearly comparable with practice than is a wet-film test in respect to such factors as condition and thickness of film, pigment concentration in the film, and brightness of the paint. The effect of brightness of the paint on hiding power is pronounced (*2, 8*) and paints undergo various and, at times, considerable changes in brightness in drying.

Experimental

Wet-Film Complete Hiding. Two wet-film brush-out tests were employed which differed only in background used. Background 1 was a checkerboard of 2.54-cm. black and white squares printed on glossy photographic paper 27.9 × 33 cm. This size was employed to make the test as nearly as possible comparable with the other complete hiding tests. Background 2 was a diamond of 1.4-cm. alternate light and dark bands printed on heavy paper and machine-coated with nitrocellulose lacquer. The design had external dimensions of 22.9 × 34 cm. and was surrounded by a clear 1.4-cm. border to make a total painting area of 929 sq. cm. Brightnesses of the areas used were:

	Background 1	Background 2
Light	80	75
Dark	5	40

Paint was applied by brush in each case until the design was no longer visible under a 75-watt daylight bulb in a white conical reflector 3 feet (90 cm.) above the test piece. Observation was at about 45° and from a distance of 3 to 4 feet. Hiding power was calculated in square centimeters per cubic centimeter from the weight of paint required to obliterate the contrast (determined by loss in weight of can and brush combination) and in square centimeters per gram of pigment.

The dry-film tests were carried out on design 2, described above. Three types of test were used: complete hiding, spreading rate at 2 per cent contrast, and a new method for hiding-power comparisons at incomplete hiding.

Dry-Film Complete Hiding and 2 Per Cent Contrast. Successive coats of each paint were applied to several charts to give increasing weight of paint until a point was reached at which contrast was no longer visible under the conditions of observation employed for the wet-film tests. The brushouts were graded by a Weston photronic cell using apparatus essentially as described by Kraemer and Schupp (*6*). Spreading rates at 2 per cent contrast were read from the curves relating contrast and film thickness for these charts.

Dry-Film Incomplete Hiding. Paints were applied to the charts at controlled spreading rates ranging from 150 to 450 sq. cm. per cc. Paint was taken up in a syringe and weighed in the syringe with a brush wet with the paint. The paint was spread over the design with the syringe and then brushed out in a standard manner. Weight of paint applied was determined as the loss of weight of the syringe and brush combination. Several charts were made of each paint. For some of the paints series of brushouts were made showing more or less uniform steps of increasing paint weight on the charts for use as arbitrary grading standards. Intervals of 0.5 to 1.0 cc. are most convenient.

Gradings were carried out on a board illuminated by four 200-watt daylight bulbs in industrial reflectors and mounted about 3 meters from the board. Illumination was vertical to the charts and uniform over the board at about 16 foot-candles. Gradings were by four observers seated below the lamps in the shadow and viewing the charts at eye level and at about 30° from the perpendicular to the charts.

In grading, the brushouts from one paint were numbered consecutively and used as arbitrary standards. A brushout from another paint was placed at the center of the grading board. Consecutive brushouts of the standard were found, one of which showed more contrast than the sample and the other less. The position of the sample in the contrast interval was then estimated in tenths of the contrast interval. Gradings made with the higher standard at the right

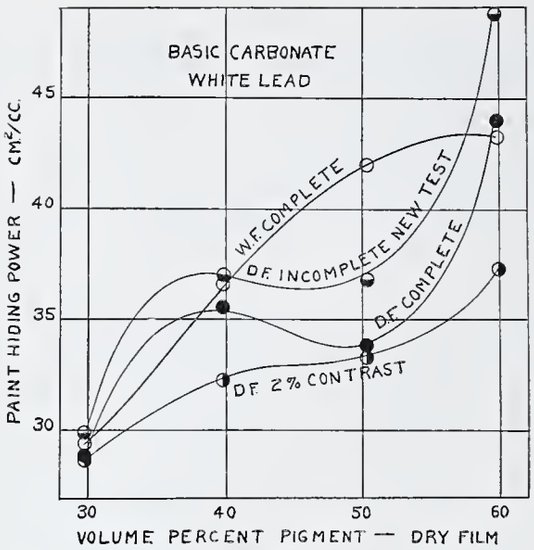

FIGURE 1

and left were averaged. Assuming the change in contrast over the film thickness interval taken to be linear, the weight of standard paint or pigment equivalent to the known weight of the sample was calculated as weight on lower standard plus difference in weight of standards times grading in tenths.

$$\text{Then hiding power for paint} = \frac{\text{equivalent weight}}{\text{sample weight}} \times \frac{\text{specific gravity sample}}{\text{specific gravity standard}} \times 100$$

$$\text{Hiding power for pigment} = \frac{\text{equivalent weight (pigment)}}{\text{sample weight}} \times 100$$

which are purely relative values indicating by how much the sample is better or poorer than the standard.

For purposes of comparison these results were converted to square centimeters per gram or square centimeters per cubic centimeter, using values of 43.7 sq. cm. per cc. and 45.8 sq. cm. per gram for lithopone paint H (Tables II and III) obtained by the complete-hiding dry-film test designated as No. 2 complete.

Since a wide range of hiding power was covered, several standard series were required. Intercomparisons between standards were made and the results finally calculated to a single standard.

This test is simple to carry out and has the very definite advantage that a permanent record may be kept.

Although four observers were used for grading, this number is not necessary. A study of agreement of observers for a group of 42 graded charts showed the average deviation of the individual grading from the mean of the group to be 1.2 per cent in terms of hiding power. The most serious individual disagreement was a deviation of 6.2 per cent.

Reproducibility is also good. An analysis of brushouts on 74 paints brushed out by five operators shows the following results:

TABLE I. REPRODUCIBILITY OF BRUSHOUTS

Operator	Paints	Average Deviation	Maximum Deviation
		%	%
A	16	1.62	3.76
B	13	1.30	5.58
C	13	1.97	5.56
D	15	1.36	4.73
E	17	1.74	4.76
		Av. 1.6	

Three brushouts were made of each paint. Deviation was from the mean of three brushouts in each case.

PAINTS. The paints used were single pigment paints using a kettle-bodied linseed oil–China wood oil combination vehicle. The pigments were titanium dioxide, lithopone (enamel type), and white lead. The paints were formulated to give definite pigment binder ratios and adjusted to equal consistency by addition of volatile. The wet paints were therefore similar in general appearance.

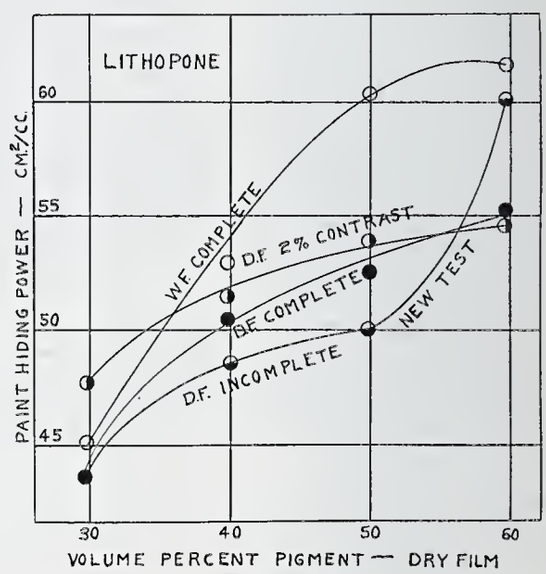

FIGURE 2

In Tables II and III the fifth and sixth columns show difference in hiding power of the wet film due to differences in contrast and design. We learn from the work of Kraemer and Schupp (*6*) that minimum perceptible contrast is greater for the checkerboard than for the narrow band type of design. In spite of this, hiding powers are greater over the latter design because of the lesser contrast to be covered up. The absolute values obtained by these tests can serve only for vertical intercomparison to indicate relative excellence. Horizontal differences between data show differences due to method of test.

TABLE II. HIDING POWER OF PAINTS

Paint	Pigment	Per Cent Pigment (Volume) Wet	Per Cent Pigment (Volume) Dry	Hiding Power: Wet Film 1[a]	Wet Film 2[b]	Dry Film 2, Complete[c]	Dry Film 2,2%[d]	New[e] Test
				Sq. cm./g.	*Sq. cm./g.*	*Sq. cm./g.*	*Sq. cm./g.*	*Sq. cm./g.*
A	BCWL	35.3	59.7	40.7	43.2	43.9	74.6	48.8
B	BCWL	31.0	50.2	37.5	42.0	33.9	66.5	36.8
C	BCWL	26.3	39.7	34.6	36.6	35.6	64.5	37.1
D	BCWL	20.5	29.6	29.7	29.4	29.0	57.4	29.9
E	Lithopone	35.4	59.7	53.0	61.6	55.2	109.0	60.1
F	Lithopone	32.6	49.9	51.3	60.4	52.5	107.7	50.1
G	Lithopone	28.0	39.8	42.7	53.0	50.6	103.1	48.6
H	Lithopone	22.1	29.7	39.5	45.9	43.7	95.5	43.7
I	TiO_2	28.8	59.8	96.2	115.8	110.2	273.6	142.3
J	TiO_2	26.5	49.8	87.6	105.8	88.6	183.1	91.5
K	TiO_2	24.0	39.8	82.9	102.1	70.9	158.5	79.0
L	TiO_2	20.3	29.7	82.5	99.1	74.8	179.9	86.9
M	TiO_2	16.2	21.6	63.8	85.6	77.3	186.5	88.8
N	TiO_2	11.5	14.3	60.1	78.3	66.3	158.3	77.5

[a] Black and white checkerboard, wet-film complete hiding.
[b] Gray and white chart, wet-film complete hiding.
[c] Gray and white chart, dry-film complete hiding.
[d] Gray and white chart, dry film 2 per cent contrast.
[e] Gray and white chart, dry film graded at incomplete hiding and converted to complete hiding value.

While the two wet-film tests tend to give generally parallel results, these results are quite different from the results by dry-film tests which also give parallel results among themselves. In Figures 1 to 6 hiding power of paint or pigment is shown as a function of volume concentration of paint in the film. Here are plotted all data over the gray and white diamond background. For simplification in plotting, the actual values obtained at 2 per cent contrast have in each case been divided by 2.

Figures 1 to 3 show paint hiding powers. Significant differences between wet- and dry-film hiding powers are noted. The trends of changes in hiding power as pigment concentration increases are different. The dry film indicates a point of inflection at intermediate pigment concentration which is entirely missed in the wet film. In the case of titanium dioxide (Figure 3) this inflection is so extreme that the hiding power of the paint actually is impaired by the addition of pigment over a portion of the range. Although it is possible that a case of this sort is unusual, nevertheless it represents a situation which requires the use of a dry-film hiding-power test. A wet-film test would be an unsafe guide in paint formulation.

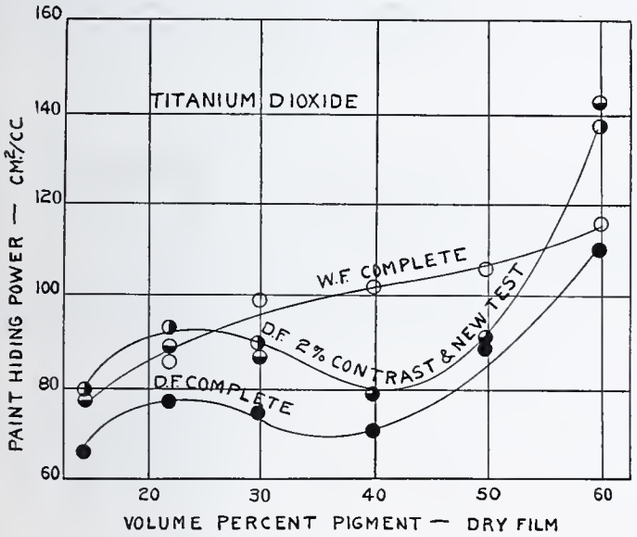

FIGURE 3

The data are even more striking in Figures 4 to 6, showing pigment hiding powers. Here the wet-film hiding powers are plotted against actual concentration in the film tested and also as a dotted line against concentration in the wet film. The latter relation is shown for easy comparison of hiding powers obtained by wet- and dry-film tests on the same paint. It is obvious that there can be no direct relation between wet- and dry-film hiding power of the pigment if hiding power is a function of concentration of pigment in the film, unless the paint contains no volatile thinner.

The data clearly show hiding power of the pigment to be a function of the concentration. Since the presence of volatile in the wet film has pronounced effect on concentration of pigment in the film, we expect and find no definite relation between wet- and dry-film hiding powers of the same paint. Because of low specific gravity, volatile thinner occupies considerably more volume than its weight per cent in the paint appears to indicate.

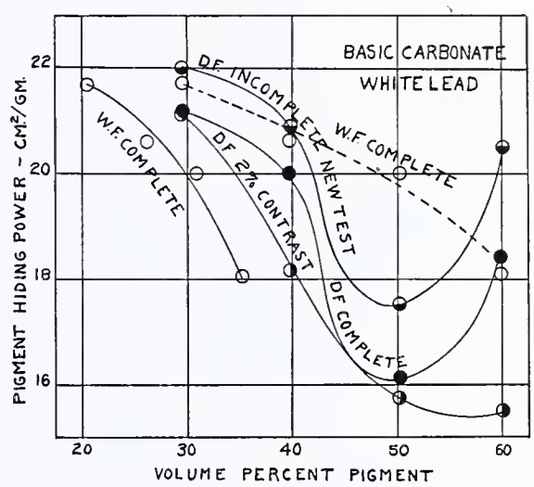

FIGURE 4

Pigment hiding power increases as concentration of the pigment decreases from a moderately high value, and represents an increase of efficiency of utilization of the pigment that is probably primarily due to increased separation of particles and consequent improved dispersion. At comparable concentration pigment hiding power is lower in a wet film than in a dry film in the cases presented here. The lower refractive index of a vehicle containing volatile probably is insufficient to make up for poorer dispersion.

One very important use made of hiding-power data at the present time is for the comparison of pigments, for which ratios of hiding powers rather than single absolute values are of primary significance. Since pigment hiding power is dependent upon concentration of pigment in the paint film, it follows that no single value can be assigned to a pigment without a recognition of the limitations of its meaning. This is particularly true of the high hiding pigments such as titanium dioxide. Several reports on hiding power investigations in the literature have shown titanium dioxide to have about twice the hiding power of lithopone.

In the group of paints here reported titanium dioxide shows from 1.7 to 4.9 times the hiding power of lithopone and 3.5 to 11.7 times the hiding power of white lead. This is a wide range, but the upper value is by no means a limiting one. The two to one relation frequently reported is based upon a comparison of paints of equal mobility in which the binder-volatile ratio is constant. Such paints are grossly different in commercial value and do not represent a practical basis for comparison. A more practical comparison is obtained in paints of equal hiding power, where tests will in general show titanium dioxide to have at least four times the hiding power of lithopone.

TABLE III. HIDING POWER OF PIGMENTS

Paint	Pigment	Per Cent Pigment (Volume) Wet	Per Cent Pigment (Volume) Dry	Hiding Power: Wet Film 1	Wet Film 2	Dry Film 2, Complete	Dry Film 2, 2%	New Test
				Sq. cm./g.	*Sq. cm./g.*	*Sq. cm./g.*	*Sq. cm./g.*	*Sq. cm./g.*
A	BCWL	35.3	59.7	17.1	18.1	18.4	31.0	20.5
B	BCWL	31.0	50.2	17.8	20.0	16.1	31.5	17.6
C	BCWL	26.3	39.7	19.5	20.6	20.0	36.3	20.9
D	BCWL	20.5	29.6	21.9	21.7	21.2	42.2	22.0
E	Lithopone	35.4	59.7	34.4	40.3	36.0	72	39.2
F	Lithopone	32.6	49.9	36.2	42.9	37.2	76	35.5
G	Lithopone	28.0	39.8	35.8	44.0	41.9	87	40.3
H	Lithopone	22.1	29.7	41.1	48.2	45.8	100	45.8
I	TiO_2	28.8	59.8	85	104	102	244	125
J	TiO_2	26.5	49.8	84	103	86	177	88
K	TiO_2	24.0	39.8	88	110	77	169	85
L	TiO_2	20.3	29.7	104	126	99	228	111
M	TiO_2	16.2	21.6	104	136	127	295	146
N	TiO_2	11.5	14.3	137	177	152	352	173

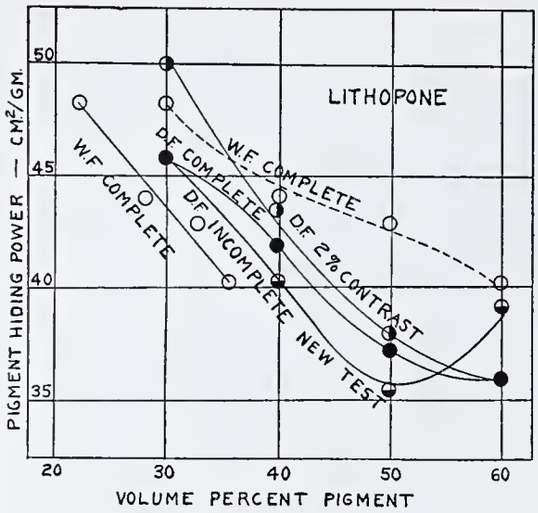

FIGURE 5

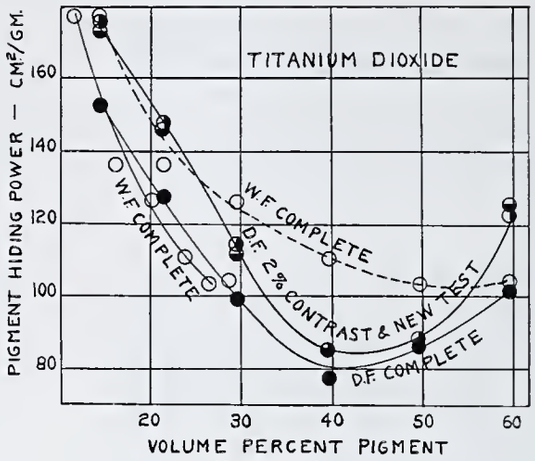

FIGURE 6

The spreading rate at 2 per cent contrast is very nearly twice the absolute hiding power at complete hiding as determined in this group of tests. This value, however, is probably closer to the practical value of the paint than is the complete hiding value, because under practical conditions paint is rarely required to cover up a background so easily seen through the film. Kraemer and Schupp (*6*) find that the least perceptible contrast increases considerably when the contrast line is not sharp and may reach a value of nearly 2 per cent under the conditions they studied. For comparing paints or pigments it should be desirable to approximate the least perceptible contrast under practical rather than extreme conditions.

Although the hiding powers reported have been determined at one-coat thickness by the new incomplete hiding method described, the method has also been employed for comparing paints at two or more coats and up to complete hiding over this background. It is easy to distinguish small differences in hiding power at contrasts between 1 and 2 per cent and even to make gradings at contrasts below 1 per cent and thus actually to see differences in paints over the design used at contrasts beyond complete hiding for less rigorous backgrounds. This is, in principle, similar to a method described by Haslam (*5*) except that visibility beyond "complete" hiding is secured by use of a more easily distinguished background rather than by alteration of the color temperature characteristics of the source of illumination.

Acknowledgment

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Comparative Clarification of Sugar Solutions

Copper Reduction and Iodine Titration Methods

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THE recent use of the iodine reduction method in the analysis of honey (*8*) and in plant materials (*10, 12*) raises the question of the effect of various clarification and clearing methods on the determination. The use of the iodine method for dextrose broadens the problem of clearing solutions for sugar analysis.

Many studies have been reported on the various methods of clarification and subsequent clearing. Englis and Tsang (*4*) reported that with clarification with basic lead acetate the deleading with disodium phosphate appears to be most satisfactory. The work of Loomis (*7*) confirms that of Bryan (*2*) showing that the use of basic lead acetate results in the loss of some of the reducing sugars, probably through the formation of a less soluble lead oxide–sugar combination. This loss did not result with the use of neutral lead acetate. On the basis of the work of Sawyer (*11*), Eynon and Lane (*5*), and Mead and Harris (*9*), Loomis (*7*) used potassium oxalate as the deleading agent and found it convenient and satisfactory. Sodium oxalate instead of potassium oxalate may be preferable because of its lower solubility. Sodium oxalate has been tentatively adopted by the Association of Official Agricultural Chemists (*1, 15*).

Inasmuch as Englis and Tsang (*4*) studied the effect of the various deleading agents with basic lead acetate only, and Loomis (*7*) in comparing basic and neutral lead acetates used potassium oxalate only, it appeared desirable to compare the use of disodium phosphate, potassium oxalate, and sodium oxalate with both the basic and neutral acetates.

The previous studies have employed only copper reduction methods of estimating the reducing sugars. Consequently a comparison was made of these several factors with both the copper reduction and iodine titration under the same laboratory conditions.

Experimental

All determinations were made on a standard invert sugar solution.

Inversion was obtained by mixing 100 grams of sugar with 30 ml. of distilled water, heating to boiling, adding 0.10 gram of crystalline tartaric acid previously dissolved in 3 ml. of distilled water, covering and boiling very slowly for 10 minutes, and cooling. Dilutions were made containing approximately 0.380 gram of invert sugar per 100 ml. of solution; 50-ml. aliquots were used for each determination, the lead compound being added to the aliquot (followed by filtration if cloudy). The lead was then precipitated by the desired deleading agent and the solution filtered. A saturated solution of neutral lead acetate was employed, 2.0 or 2.5 ml. being used for a determination. Varying quantities of the basic lead acetate (Horne's) were employed. Quantities of solid disodium phosphate, potassium oxalate, and sodium oxalate just sufficient to effect complete precipitation of the dissolved lead were added. The copper reduction method was that of Shaffer and Hartman (*13*), and the iodine oxidation method was that of Lothrop and Holmes (*8*).

Results and Discussion

The data are given in Table I. In general neutral lead acetate and sodium oxalate constitute the most satisfactory combination of clarifying agents for both the iodine oxidation and copper reduction methods. Complete recovery of the dextrose was obtained with the iodine method and 99.7 per cent recovery with the copper method.

Table I. Comparison of Copper Reduction and Iodine Oxidation Estimations of Clarified Reducing Sugar Solutions

Iodine Oxidation				Copper Reduction			
Blank dextrose	Recovered dextrose	Recovery	Loss	Blank reducing sugars	Recovered reducing sugars	Recovery	Loss
Mg.	*Mg.*	%	%	*Mg.*	*Mg.*	%	%
2.5 ml. of saturated neutral lead acetate + potassium oxalate							
94.4	93.9	99.5	0.5	188.8	186.4	98.7	1.3
94.4	93.7	99.3	0.7	188.8	186.5	98.8	1.2
2.0 ml. of saturated neutral lead acetate + potassium oxalate							
99.6	98.9	99.3	0.7	99.6[a]	98.2[a]	98.6	1.4
99.6	98.6	99.0	1.0	99.6[a]	98.0[a]	98.4	1.6
2.5 ml. of saturated neutral lead acetate + sodium oxalate							
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
94.4	94.4	100.0	0.0	188.8	188.0	99.5	0.5
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
2.5 ml. of saturated neutral lead acetate + disodium phosphate							
94.4	83.3	88.3	11.7	188.8	187.3	99.2	0.8
94.4	83.5	88.5	11.5	188.8	187.1	99.1	0.9
94.4	82.9	87.8	12.2	188.8	186.8	98.9	1.1
94.4	83.1	88.0	12.0	188.8	187.1	99.1	0.9
2.0 ml. of saturated neutral lead acetate + disodium phosphate							
99.6	90.7	91.1	8.9	99.6[a]	98.2[a]	98.6	1.4
99.6	91.1	91.5	8.5	99.6[a]	98.3[a]	98.7	1.3
0.17 gram of basic lead acetate + potassium oxalate							
95.5	95.3	99.8	0.2	191.0	183.4	95.1	4.9
95.5	95.1	99.5	0.5	191.0	183.6	95.2	4.8
0.34 gram of basic lead acetate + potassium oxalate							
95.5	94.9	99.4	0.6	191.0	180.5	94.5	5.5
95.5	94.7	99.2	0.8	191.0	180.3	94.3	5.7
0.50 gram of basic lead acetate + potassium oxalate							
95.5	94.5	99.0	1.0	191.0	177.1	92.7	7.3
95.5	94.7	99.2	0.8	191.0	177.0	92.7	7.3
1.0 gram of basic lead acetate + potassium oxalate							
99.6	92.3	92.7	7.3	99.6[a]	91.8[a]	92.2	7.8
0.17 gram of basic lead acetate + sodium oxalate							
95.5	95.5	100.0	0.0	191.0	185.0	96.9	3.1
95.5	95.3	99.8	0.2	191.0	184.5	96.6	3.4
0.34 gram of basic lead acetate + sodium oxalate							
95.5	94.9	99.4	0.6	191.0	181.0	94.7	5.3
99.5	95.1	99.5	0.5	191.0	181.1	94.7	5.3
0.50 gram of basic lead acetate + sodium oxalate							
95.5	95.3	99.8	0.2	191.0	179.2	93.7	6.3
95.5	95.3	99.8	0.2	191.0	179.2	93.8	6.2
Less than 0.1 gram of basic lead acetate + disodium phosphate							
94.4	93.9	99.5	0.5	188.8	187.3	99.1	0.9
94.4	93.8	99.4	0.6	188.8	187.1	99.0	1.0
0.15 gram of basic lead acetate + disodium phosphate							
94.4	93.1	98.6	1.4	188.8	187.1	99.0	1.0
94.4	92.9	98.4	1.6	188.8	186.8	98.9	1.1
0.5 gram of basic lead acetate + disodium phosphate							
95.5	93.0	97.4	2.6	191.0	184.0	96.3	3.7
95.5	93.2	97.6	2.4	191.0	184.0	96.3	3.7

[a] Dextrose.

Neutral lead acetate and potassium oxalate are only fairly satisfactory in the iodine method, 99.3 to 99.5 per cent recovery of dextrose being observed. Basic lead acetate and sodium oxalate are apparently quite satisfactory in the iodine method, 99.8 per cent of the dextrose being recovered. The use of basic lead acetate and either potassium oxalate or disodium phosphate resulted in losses of 0.5 to 7.3 per cent of dextrose, varying with the increase in basic lead acetate from 0.1 to 1.0 gram (per 50 ml. of test solution). The use of neutral lead acetate and disodium phosphate resulted in losses ranging from 11.5 to 12.2 per cent.

As above, the use of neutral lead acetate and sodium oxalate with the copper reduction method is satisfactory, an average of 99.7 per cent of the dextrose being recovered. All other methods resulted in losses of 0.8 to 7.8 per cent. These results confirm in general and extend those of the many previous studies and also provide a source of comparison. The difference in effectiveness of potassium and sodium oxalate with neutral lead acetate is marked, losses ranging from 0.5 to 1.0 per cent with the potassium salt to slightly over 0.3 per cent with sodium oxalate.

The marked buffering effect of the phosphate on the iodine reaction is evident in the two series with neutral lead acetate and disodium phosphate. In both cases there is a distinctly high loss of recovered dextrose (8.5 to 12.2 per cent) in the iodine titration. This loss would be expected on the basis of the lower hydroxyl-ion concentration in the phosphate solutions, incomplete oxidation occurring in such solutions (*3, 6, 14*) under the conditions of the determination.

Summary

Solutions of invert sugar analyzed by the copper reduction and iodine oxidation methods are most satisfactorily clarified by neutral lead acetate and sodium oxalate, complete recovery of dextrose being observed with the iodine method and 99.7 per cent recovery with the copper method.

Other methods were less satisfactory, though with the iodine method, using neutral lead acetate and potassium oxalate or basic lead acetate and sodium or potassium oxalate, recoveries of 99.5 to 99.8 per cent of dextrose were observed.

All methods except that with neutral lead acetate and sodium oxalate resulted in losses of 0.8 to 7.8 per cent of dextrose or reducing sugars determined by the copper reduction method.

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Detection and Estimation of Small Amounts of Fluorine

Application of the Zirconium Purpurin Test

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The qualitative test for fluorine described uses a modification of the de Boer-Basart reagent and is sensitive to 0.003 mg. of fluoride. Various anions have an interfering effect. A simple distillation method is described by which 0.005 mg. of fluorine can be detected in the presence of any cation or anion.

A procedure for the titration of 0.5 to 15 mg. of fluorine, using zirconium oxychloride as reagent and purpurin as indicator, is given which is accurate to 2 per cent. A colorimetric method for quantities of fluorine between 0.01 and 0.05 mg. is also described which is accurate to 0.002 mg. of fluorine. In the presence of interfering substances the fluorine is separated by a distillation method.

The increasing interest in the occurrence of traces of fluorine in natural products demands a simple, specific, and sensitive test for the detection and estimation of this element. Of the various methods mentioned in the literature, the method of de Boer and Basart (*4, 5*) seemed the most promising. The method has been modified and extended by Pavelka (*9*), Alimarin (*2*), Koone (*8*), Willard and Winter (*14*), and Armstrong (*3*). However, most of their methods are applied to neutral or feebly acid solutions, thereby losing the inherent advantage of the de Boer-Basart method which is applied in a strong hydrochloric acid solution. In solutions of high acidity considerably fewer substances interfere, and often a long separation of the fluorine from these interfering substances can be eliminated. The present method uses an 8 *N* hydrochloric acid solution.

In attempting to determine the fluorine content of standard ammonium and sodium fluoride solutions by the calcium fluoride method, highly variable results were obtained. Better results were obtained as follows:

To 25 cc. of ammonium fluoride containing 1 to 2 per cent of fluorine and a few drops of ammonium hydroxide strontium chloride solution was slowly added with constant stirring. The filtered strontium fluoride was washed with saturated strontium fluoride solution, dried, ignited, and weighed. In this way a solution was found to contain 1.253, 1.253, 1.254, and 1.255 per cent of fluorine. Sometimes a precipitate formed which could not be filtered. However, when filtration was possible, consistent results were obtained and the procedure is superior to the calcium method.

Three different samples of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) were used, one obtained from de Boer, one purchased from the City Chemical Company, and one from the Welsbach Company. The latter was very impure, even after an ether extraction to remove the ferric chloride. The zirconium content of the City Chemical Company product was found to be 28.2 per cent (phosphate method) and 28.3 per cent (precipitation as hydrous oxide and weighing as ZrO_2), respectively (calculated, 28.25 per cent). This product was mainly used in the following work.

The purpurin used was a Kahlbaum product, recrystallized from alcohol.

Qualitative Test

The following substances are necessary to make one liter of the reagent: 0.16 gram of zirconium oxychloride, 9 mg. of purpurin (1,2,4-trihydroxyanthraquinone), 30 cc. of ethanol, and 720 cc. of concentrated hydrochloric acid.

The zirconium salt is dissolved in 100 cc. of concentrated hydrochloric acid, 100 cc. of water being added to insure a clear solution. The purpurin is dissolved in the alcohol and the resulting solution added slowly with continuous shaking to the zirconium solution. The remainder of the hydrochloric acid is then added and the solution made up to 1 liter with water. It is essential that the purpurin be added to the zirconium solution and not vice versa, since otherwise the solution becomes cloudy. The mixture is allowed to stand overnight and is then ready for use. The reagent is stable for at least 1 month. After 2 or 3 months the color begins to fade and a precipitate forms.

In the absence of interfering substances, the solid, or residue obtained after evaporating the solvent, is dissolved in 2 cc. of 6 *N* hydrochloric acid and 2 cc. of the reagent are added. The pink color of the reagent will turn yellow immediately if 0.003 mg. or more of fluoride is present. To confirm the presence of fluorine, solid zirconium oxychloride is added a little at a time with shaking. The color should turn pink again. If it does not, or if a cloudy or orange solution results after the addition of the purpurin-zirconium reagent, the presence of interfering elements which have destroyed the dye is indicated. The final acidity of the mixture should be between 7 *N* and 10 *N* with respect to hydrochloric acid. If the acidity is greater than 10 *N*, the color in the absence of fluorine is orange or yellow; if less than 6 *N*, a cloudy solution forms. The test becomes impossible at acidities of less than 4 *N*.

De Boer and Basart (*4, 5*) mention sulfuric and oxalic acids as interfering, and Stone (*12*) describes the interference of phosphoric acid. Phosphates cause the solution to become cloudy in a short time by precipitating the insoluble zirconium phosphate. Borates have no influence alone, but prevent the formation of the yellow color in the presence of fluoride, unless the fluoride is present in excess. Nitrates do not interfere immediately, but upon long standing the dye is destroyed. Strongly oxidizing substances (chlorates, bromates, iodates, etc.) evolve chlorine and destroy the dye, but can be rendered harmless with sulfurous acid. Complex fluorides as fluosilicates and borofluorides behave like fluorides. It is evident that the direct color test is fairly limited. Generally, a separation according to distillation or precipitation is recommended.

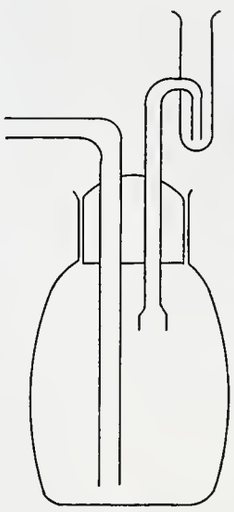

Figure 1

Distillation Method. The fluoride is distilled off as silicon tetrafluoride, which is collected in the pink purpurin-zirconium reagent. The distillation apparatus consists of a wide-mouth Pyrex flask of about 150 cc. capacity. It is

fitted with a ground-glass stopper (Figure 1) containing an inlet tube extending to the bottom and a second tube ending below the neck of the flask, the other end of which is bent down and sealed in a small test tube.

The dry sample is introduced into the flask with about 1 gram of quartz or silica powder and 25 cc. of concentrated sulfuric acid. One cubic centimeter of the purpurin-zirconium reagent is put into the small test tube. A stream of air, dried through concentrated sulfuric acid, is passed through the flask and the latter heated to 140° C. in an oil bath. It is essential that the entire apparatus be perfectly dry before the test is begun. The temperature should never exceed 160° C. A blank test run for 1 hour without any fluoride gave no change in color of the reagent in the small test tube. Longer heating resulted in a gradual change of color of the reagent to orange. The speed with which the reagent changes color depends on the amount of fluoride present as shown in Table I.

Table I. Detection of Fluoride by Distillation Method

Fluorine	Time	Color of Reagent	Fluorine	Time	Color of Reagent
Mg.	*Min.*		*Mg.*	*Min.*	
1.0	0.33	Yellow	0.01	15	Orange
0.1	1	Yellow	0.01	20	Yellow
0.05	3	Yellow	0.005	30	Orange-yellow
0.03	3	Orange	0.005	40	Yellow
0.03	5	Yellow			

The test is sensitive to 0.005 mg. of fluorine with a time of heating of 40 minutes. With 0.0025 mg. of fluorine and 50 minutes of heating the reagent had become orange-yellow.

Phosphates, bromides, chlorides, sulfates, sulfites, acetates, oxalates, sulfides, and cations do not interfere. Boric acid in the absence of fluoride turns the reagent an orange color which is easily distinguished from the yellow color obtained with fluorides. It is easy to detect as little as 0.01 mg. of fluorine in the presence of 500 mg. of boric acid. Nitrates and nitrites interfere and destroy the purpurin in the reagent, which turns cloudy yellow. Interference by nitrates and nitrites can be eliminated by dissolving some salicylic acid in the sulfuric acid used, thus transforming the acids into nitro and nitroso compounds. It is recommended to add the sulfuric and salicylic acid mixture at a low temperature (flask in ice) in order to prevent volatilization of silicon fluoride. In the presence of 500 mg. of nitrate or nitrite 0.05 mg. of fluoride could be detected.

Chlorates, bromates, dichromates, and some other strongly oxidizing agents interfere. This interference can be eliminated by adding a little sodium bisulfite to the reagent in the small test tube. Iodide in quantities larger than 10 mg. interferes. It can be removed by adding to the aqueous solution of the sample enough silver sulfate to insure quantitative precipitation of the iodide (test filtrate with a little nitrite and acid and carbon tetrachloride). Although tartrates do not interfere in the direct test for fluoride, they exert an interfering effect in the distillation method. Probably one of the decomposition products formed on heating with sulfuric acid forms a stable complex with the zirconium, causing the color change of the reagent from pink to yellow. Tartrate can be made harmless by addition of enough ferric sulfate to the sulfuric acid. The addition of 5 grams of ferric sulfate overcomes the interference caused by one gram of tartaric acid. In this way 0.01 mg. fluorine could be detected in the presence of 500 mg. of tartrate.

When iodides are present, enough silver sulfate is added to the aqueous solution of the sample to decrease the iodide content to less than 10 mg. The filtrate is made slightly alkaline and evaporated to dryness. The dry residue (or the dry sample in the absence of more than 10 mg. of iodide) is mixed intimately with several grams of quartz powder. The mixture is transferred to the distillation flask, and 5 grams of ferric sulfate are added if tartrates might be present. The flask is immersed in ice water and 50 cc. of sulfuric acid containing a few grams of salicylic acid are slowly added with vigorous shaking. (In case nitrates and nitrites are absent, the procedure described for fluoride alone should be followed, since the sensitivity in the latter case is greater). The stopper is now inserted in the flask with 1 cc. of the reagent, saturated with sulfur dioxide, present in the small attached test tube. The rest of the procedure is the same as described above.

Sensitivity, 0.005 mg. of fluorine after 40 minutes; 0.05 mg. in the presence of nitrates and nitrites.

Precipitation Method. The distillation method is the most sensitive and reliable test for the detection of fluoride in the presence of interfering anions. However, for ordinary class work it may be advantageous to have a less sensitive method not requiring special apparatus.

The solution of the unknown is acidified with hydrochloric acid in a platinum dish and heated with an excess of barium chloride. The precipitate is filtered off and washed a few times with dilute hydrochloric acid. A few cubic centimeters of 4 *N* acetic acid, a drop of methyl orange, and sodium hydroxide are added until the color of the solution corresponds to a pH of 4.5. An excess of calcium chloride is then added, followed by some ammonium oxalate. At this point the volume should not exceed 25 cc. The precipitate is filtered and washed twice with an acetate buffer of pH 3.5. The precipitate is dissolved in a few drops of concentrated hydrochloric acid, a little permanganate added to remove the oxalic acid, and the permanganate removed with an excess of sodium bisulfite. The resulting solution is tested as described in the beginning of the paper. The method is sensitive to 0.1 mg. of fluorine in the presence of interfering anions.

Stone's method (*12*) is simpler in the presence of phosphates, sulfates, and oxalates, but is less reliable than the methods described above in the presence of interfering substances.

The authors had considerable difficulty in detecting 0.03 mg. of fluorine in the presence of phosphate or sulfate by Stone's method, since there was always a certain amount of doubt as to whether the change of color was due to the fluoride on the one hand or to the phosphate or sulfate on the other. In the presence of oxalate they were unable to detect less than 0.5 mg. fluorine according to Stone's procedure.

Quantitative Estimation

Reagents required are 300 mg. of purpurin in a liter of ethanol, and 10 *N* hydrochloric acid, zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) in 10 *N* hydrochloric acid containing 0.8 gram of zirconium per liter, and a solution of 19.60 grams of cobalt nitrate [$CO(NO_3)_2 \cdot 6H_2O$] and 0.132 gram of potassium dichromate per liter water kept in a glass-stoppered bottle.

Procedure. For the determination of 0.5 to 15 mg. of fluoride the fluoride sample is introduced into an oil-sample bottle of 100 cc. capacity. If it is a solid, 2 cc. of water should be added; if it is a liquid, 2 cc., or a larger volume, made about 10 *N* with respect to hydrochloric acid together with 2 cc. water may be used. Five cubic centimeters of 10 *N* hydrochloric acid are added from a buret and then 2 cc. of the purpurin solution from a pipet. Forty cubic centimeters of the cobalt-dichromate solution measured with a graduate are put into a similar oil-sample bottle and used to give standard color for comparison. The zirconium solution in hydrochloric acid is now added from a buret until the color of the solution begins to approach that of the cobalt-dichromate standard. More 10 *N* hydrochloric acid is then added to bring the total volume just under 40 cc., more zirconium being added till the color matches that of the standard with a total volume of 40 cc. (adjusted by adding sufficient 10 *N* hydrochloric acid from the buret). The zirconium solution must be added slowly with a shaking so that the titration requires at least 1 to 2 minutes.

The number of milligrams of zirconium used is calculated and 1 mg. subtracted from the amount (explained below). The corresponding amount of fluoride present is read in Table II.

Table II. Fluoride Corresponding to Zirconium Used

Zirconium Used	Fluoride Present	Zirconium Used	Fluoride Present	Zirconium Used	Fluoride Present
Mg.[a]	*Mg.*	*Mg.*[a]	*Mg.*	*Mg.*[a]	*Mg.*
1	0.40	10	4.15	19	8.90
2	0.75	11	4.65	20	9.50
3	1.20	12	5.10	21	10.10
4	1.60	13	5.60	22	10.72
5	2.00	14	6.12	23	11.40
6	2.47	15	6.63	24	12.08
7	2.90	16	7.15	25	12.90
8	3.25	17	7.73	26	13.70
9	3.70	18	8.26	27	14.53
				28	15.40

[a] Minus 1 mg.

Suppose that 8.75 mg. of zirconium were used in the titration. By interpolation it is found that 7.75 mg. of zirconium correspond to 3.16 mg. of fluorine.

Table III shows that the method gives satisfactory results, even in the titration of small amounts of fluoride of the order of 1 mg.

Table III. Titration of Fluoride

Fluoride Taken	Zirconium Used (Uncorrected)	Fluoride Found	Relative Error
Mg.	*Mg.*	*Mg.*	%
0.50	2.30	0.505	+1
0.50	2.34	0.52	+4
0.60	2.50	0.575	−4
0.90	3.35	0.91	+1
0.90	3.31	0.89	−1
1.50	4.93	1.57	4
1.50	4.87	1.55	3
1.50	4.91	1.56	4
5.00	12.78	5.00	0
5.00	12.74	4.98	−0.5
5.00	12.69	4.96	−1
10.00	22.00	10.10	+1
10.00	21.75	9.95	−0.05
10.00	22.20	10.22	+2
15.00	28.8	15.23	+1.5
15.00	28.9	15.31	+2
15.00	28.55	15.01	0

Discussion

The zirconium solution should be made up in small quantities or standardized frequently, since the chloride has a tendency to precipitate out after several months of standing. The standardization can be made most conveniently against a solution of known fluoride content according to the procedure described above.

The purpurin solution in alcohol is nearly saturated. There is no danger of precipitation of dye with fluctuations in temperature. A zirconium-purpurin reagent in fairly strong hydrochloric acid is not stable and should be standardized daily. For quantitative work it was therefore considered more advantageous to keep the solutions of both reagents in separate bottles. The color standard (cobalt-dichromate) should be kept in glass-stoppered bottles. If cork stoppers are used, the solution slowly becomes more red by reduction of the dichromate.

Correction for Blank. The cobalt-dichromate standard has the same yellow-orange color as a solution containing 0.5 mg. of zirconium, 38 cc. of 10 *N* hydrochloric acid, and 2 cc. of the purpurin solution. With other amounts of zirconium, solutions are obtained varying in color from yellow to deep pink-violet. In preliminary work it was found that if samples of fluoride were titrated first to one such blank and then to another having a more red color, inconsistent results were obtained if only the weight of zirconium in the blank was subtracted from the total amount of zirconium used. By subtracting twice the weight of zirconium in the blank from each titration value, the ratio of zirconium to fluoride found was nearly the same at the different end points. Thus, by titrating to a yellow-orange color, a zirconium-fluoride ratio of 3.1 and of 3.4 was found if the titration was finished at a red-orange color. In both cases the amount of zirconium in a blank having the same color as the solution at the end point was subtracted from the titration figure. If double the amount was subtracted, the ratios found were 2.50 and 2.48, respectively.

Since the stability constants of the various complex compounds between zirconium and fluoride are not known, it is impossible at the present time to base the empirical correction on a more exact basis. The atomic ratio of fluorine to zirconium at the end point increases with increasing amounts of fluoride. With 0.5 mg. of fluoride it was found to be 1.90 increasing to 2.60 with 15 mg. of fluoride (uncorrected for blank). The following are some of the complexes reported to occur (*13*):

$$Zr_3F_{17}^{-----},\ Zr_2F_{13}^{-----},\ ZrF_5^{-},\ ZrF_6^{--},\ ZrF_7^{---}$$

It seems that in more dilute solutions complexes containing much less fluoride occur.

Effect of Temperature. If the cobalt-dichromate standard is used for comparison, the results are independent of wide fluctuations in temperature. When a color standard is used, made by adding small amounts of zirconium to hydrochloric acid and purpurin, a large temperature effect occurs, the color of the standard becoming more yellow with increasing temperature, whereas the color of the titrated solution is not affected by a fairly large change in temperature. Consequently errors of about 0.5 per cent per degree of temperature difference arise. Therefore, the use of the cobalt-dichromate standard is not only desirable but necessary if accurate results are to be obtained.

Acidity. A final acidity of 8.5 *N* with respect to hydrochloric acid has been chosen. If the acidity is lower than 6 *N* a cloudy solution results; if it is greater than 10 *N*, a poor contrast of colors occurs, the color never fully developing. The amount of zirconium used to titrate to the same end point increases with decreasing acidity; however, a slight change of the final acidity of 8.5 *N* hardly affects the results.

Cobalt-Dichromate Color Standards. The mixture selected has a yellow-orange color similar to that of a solution of 0.5 mg. of zirconium in 38 cc. of 10 *N* hydrochloric acid and 2 cc. of purpurin reagent. Under these conditions the authors noticed the most pronounced changes in color at the end point. This may be a subjective matter and other workers may prefer another color for comparison; therefore a set of various color standards is given in Table IV.

Table IV. Cobalt-Dichromate Color Standards

$Co(NO_3)_2 \cdot 6H_2O$	$K_2Cr_2O_7$	Zirconium in Blank Having Same Color	Color
Mg./40 cc.	*Mg./40 cc.*	*Mg.*	
784	5.28	0.50	Yellow-orange
784	4.00	0.64	Orange
784	3.28	0.72	Orange
784	2.52	0.80	Orange-pink
784	1.96	1.00	Pink

In using another color standard than the one recommended, it is necessary to subtract twice the amount of zirconium in the corresponding blank from the titration figure before using Table II.

Sharpness of Color Change. The color change near the end point is very gradual. For example, in the titration of 5 mg. of fluoride the solution stayed yellow until 15 cc. of zirconium reagent had been added. With 15.5 cc. the solution was faintly yellow-orange; with 16.5 cc., distinctly yellow-orange; with 17.5 cc., yellow-orange (matched blank); with 18 cc., orange; with 19.0 cc., pink-orange; and with 19.5 cc., pink. By using the comparison solution the end point was certain to 0.2 cc.

Speed of Titration. Sufficient time should be allowed for the reaction between fluoride and zirconium to become complete. If the titration is made very quickly too much zirconium is used; the end point is not permanent, and

upon standing changes to the reddish side. It is not safe to make a titration in less than 1 minute. If 2 minutes are required in the titration, the solution being shaken several times, good results will be obtained.

Determination of Microquantities. The method for titration of fluoride described cannot be used for titration of quantities of fluoride of less than 0.5 mg. A special colorimetric titration procedure is described below for amounts of fluorine between 0.01 and 0.05 mg.

The zirconium-purpurin reagent is prepared by adding slowly with shaking a solution of 9 mg. of purpurin in 30 cc. of ethanol to a solution of 0.16 gram of zirconium oxychloride in 6 *N* hydrochloric acid. Add 620 cc. of concentrated hydrochloric acid to the mixture, and make to 1 liter with water. The standard fluoride solution is a solution of sodium fluoride containing 2 mg. of fluorine per 100 cc. of 8 *N* hydrochloric acid.

Measure out 10 cc. of the zirconium-purpurin reagent into each of two test tubes of uniform diameter. Add the unknown sample made up to 2 cc. and 6 *N* with respect to hydrochloric acid to one test tube. To the other add 2 cc. of 6 *N* hydrochloric acid. Add about 2.4 cc. of the standard fluoride solution from the microburet to the second tube, which gives an orange color. Then add the same fluoride solution to the other test tube and enough 8 *N* hydrochloric acid so that the colors match when the volumes are the same.

The difference in the amount of standard fluoride added to both test tubes corresponds to the amount of fluorine in the unknown. Thus, if 2.4 cc. were used for the blank and 1.7 cc. for the sample, the fluorine content of the unknown is $(2.4 - 1.7)\ 0.02 = 0.014$ mg.

The end point can be recognized within 0.1 cc. of the standard fluoride solution—that is, the method is accurate within 0.002 mg. of fluoride. Hence, the amount of fluoride in the sample should be 0.01 mg. or larger in order to get an accuracy of at least 10 per cent. The upper limit of fluorine in the sample amounts to 0.05 mg. according to the procedure described. Larger quantities can be determined if larger tubes and more of the zirconium-purpurin reagent are used. Another alternative which has not been investigated is the use of a reagent containing more zirconium.

Experimental results are given in Table V. Some titrations were made in the presence of substances not expected to interfere.

Table V. Colorimetric Titration of Fluoride

(0.01 to 0.05 mg.)

Fluoride Taken	Substance Added (20 mg.)	Fluoride Found	Error
Mg.		*Mg.*	%
0.005	....	0.006	+20
0.005	....	0.004	−20
0.010	....	0.011	+10
0.010	....	0.010	0
0.040	....	0.040	0
0.040	....	0.038	−5
0.010	Calcium acetate	0.010	0
0.040	Calcium acetate	0.042	+5
0.010	Potassium iodide	0.009	−10
0.040	Potassium iodide	0.042	+5
0.010	Sodium sulfite	0.010	0
0.040	Sodium sulfite	0.038	−5
0.010	Sodium nitrate	0.009	−10
0.040	Sodium nitrate	0.040	0
0.010	Sodium acetate	0.010	0
0.040	Sodium acetate	0.040	0

Interfering Substances. Colored substances, substances forming chlorine with hydrochloric acid, substances precipitating with zirconium (phosphates) or forming more or less stable complexes with fluoride (aluminum, boric acid), and in addition, sulfates, oxalates, and nitrites interfere with the titration. Successful titrations have been made in the presence of nitrates, sulfites, acetates, iodides, bromides, zinc, calcium, barium, magnesium, and alkali salts.

Oxidizing substances can be reduced with sodium sulfite before the titration. Aluminum ions and boric acid tend to form complexes with fluoride. Since these complexes are less stable than the zirconium complex in the strong acid medium, titrations can be made in the presence of small amounts of these substances. In the titration of 2 mg. of fluoride 7.50 cc. of reagent were required; in the presence of 10 mg. of aluminum, 7.50; of 15 mg., 7.2; of 20 mg., 7.0; of 30 mg., 6.1; and of 50 mg., 5.5 cc., respectively. With the same amount of fluorine and 1 to 10 mg. of boric acid the results found were about 5 per cent high. The complex formation does not interfere yet or at any rate is overshadowed by a tendency of boric acid to react with the zirconium-purpurin reagent. With 100 mg. of boric acid the results were 33 per cent low. Phosphate interferes strongly; when as little as 1 mg. is present, it becomes impossible to titrate a 1-mg. sample of fluoride, owing to the cloudy appearance of the solution.

The distillation as H_2SiF_6 according to the method of Willard and Winter (*14*) can be used to separate fluorine from these interfering substances, or the fluorine can be distilled off as silicon tetrafluoride by the well-known method described by Daniel (*7*), Adolph (*1*), Reynolds (*10, 11*), Cesares (*6*), and others. Using the latter method, a number of determinations were made, using the simple apparatus described above. (Further details are given in the thesis of Stansby.) The results are tabulated in Table VI. Good results were obtained only with an extremely slow rate of heating during the distillation, a point not brought out in the literature.

Table VI. Determination of Fluoride in the Presence of Various Substances

Fluoride Taken	Other Substances Present	Fluoride Recovered	Remarks
Mg.		%	
5	NaAc, NaBr, NaCl, NaS_2O_3, $K_2Cr_2O_7$, 50 mg. of each	60, 51	Collected in water
5	NaAc, NaBr, NaCl, $Na_2S_2O_3$, $K_2Cr_2O_7$, 50 mg. of each	97, 98, 100, 101	Collected in NaOH
5	KH_2PO_4, 500 mg.	97, 100	Collected in NaOH
5	$AlCl_3$, 200 to 500 mg.	(57), 98, 98, 99, 100	Collected in NaOH
5	H_3BO_3, 250 mg.	1, 7	Collected in NaOH
5	H_3BO_3, 10 mg.	64, 80	Collected in NaOH
5	$NaNO_2$, 500 mg.	97, 98	Distillate with sulfite
5	$NaNO_3$, 500 mg.	95, 96	Distillate with sulfite
5	KI, 500 mg.	97, 98, 102	Distillate with sulfite
5	$KClO_3$, 200 mg.	99, 99	Distillate with sulfite
5	$Na_2C_2O_4$, 500 mg.	95, 98, 100	Distillate with sulfite
2	KH_2PO_4, $AlCl_3$, NaAc, NaBr, $NaNO_3$, $NaNO_2$, 50 mg. of each	(56), 94, 97, 98, 101	Distillate with sulfite
0.1	$Na_2C_2O_4$, KH_2PO_4, KCl, 500 mg. of each	95, 95	Distillate with sulfite
0.1	$NaNO_3$, $NaNO_2$, $KClO_2$, 50 mg. of each	100, 105, 95	Distillate with sulfite

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Acidity Titration of Low-Grade Rosins

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In determining the acid number of rosin it is the general procedure to dissolve 1 to 2 grams of the sample in 50 cc. of neutral 95 per cent alcohol, add phenolphthalein as indicator and titrate with 0.5 *N* standardized aqueous potassium or sodium hydroxide solution. The acid number is the number of milligrams of potassium hydroxide required to neutralize 1 gram of sample. With the higher grades of rosin little difficulty is experienced in determining the end points, although the solution becomes slightly redder as the end point is neared. However, with low-grade rosins the red color of the solution almost completely masks the end point, resulting in unreliable acid numbers.

By using a modification of the Albert method, Coburn (*3*) was able to duplicate results very closely in the titration of low-grade rosin. His method consists in dissolving a 1- to 2-gram sample in 25 cc. of 2 to 1 benzene-alcohol mixture, adding 25 cc. of saturated sodium chloride solution, and several grams of sodium chloride, and then adding an excess of 0.5 *N* aqueous alkali. The uncombined alkali goes into the brine layer and is titrated back with standardized acid solution. Phenolphthalein is used as indicator. This method is based upon the insolubility of rosin soap and the solubility of alkali in the brine layer. However, the writer was not able to duplicate results with low-grade rosin because the end point was masked by the red color of the salt solution, caused by the soap of the highly oxidized portion of the rosin, which could not be salted out.

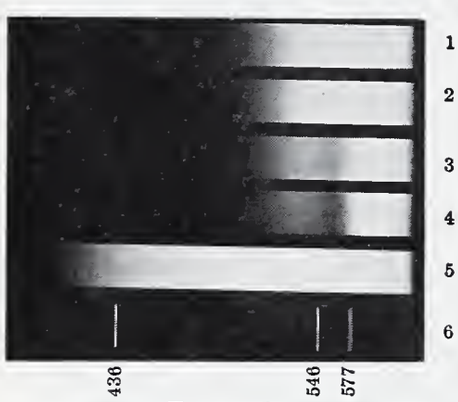

Figure 1

An examination of the absorption spectra of phenolphthalein and rosin solutions suggested a method of detecting the end point of the titration. By using a small direct-vision hand spectroscope, the first appearance of the phenolphthalein absorption band in a certain thickness of a solution of low-grade rosin in alcohol furnished a more sensitive criterion for the end point of the titration than attempting to note a color change.

It has been shown by Brode (*2*) that phenolphthalein in solutions of 8.4 to 10.0 pH possesses a relatively narrow absorption band in the green with maximum absorption at wave-length 553 mμ, the more alkaline solutions showing stronger and broader absorption. Müller and Partridge (*4*) have made use of the characteristic absorption bands of phenolphthalein and other indicators in titrating with photoelectric cells. Brice (*1*) has shown that the absorption of light by rosins is practically continuous, the region of complete absorption shifting toward the red as the grade of the rosin becomes lower. For example, G rosin type (0.875 inch (2.22 cm.) thickness of rosin) absorbs all wave-lengths shorter than about 530 mμ, while F rosin type absorbs completely all wave lengths below about 560 mμ. The absorption spectra of rosin solutions are similar to those of rosins, and to show any effect due to the phenolphthalein the rosin solution must have such a concentration and/or thickness that its color is not redder than about a G rosin. With the concentration fixed by other considerations, the optimum thickness of solution for observing the presence or absence of the phenolphthalein absorption band is 0.5 to 1 inch (1.26 to 2.5 cm.).

The feasibility of using the first detectable appearance of the phenolphthalein absorption band as the end point in titration of rosins was first tested out on a solution of a high-grade rosin, so that a comparison could be made with the end point as determined by color change.

Five grams of WG rosin and 1 cc. of 1 per cent alcoholic solution of phenolphthalein were dissolved in 100 cc. of 95 per cent alcohol in a 300-cc. Erlenmeyer flask, and 0.5 *N* aqueous sodium hydroxide was added until a faint pink indicated the end point. The solution was then examined with the hand spectroscope, the sky being used as a background. The phenolphthalein absorption band, though detectable through about 3 inches (7.5 cm.) of solution, could not be seen through a 1-inch (2.5-cm.) layer of solution. However, the addition of 0.1 cc. excess alkali made the absorption band visible even through a 0.5-inch (1.26-cm.) layer. Similar results were obtained on N and M rosin.

This procedure was then extended to solutions of low-grade rosins, for which the color end point is masked but for thin layers of which the phenolphthalein absorption band is not masked. Five grams of B rosin (rosin redder than D type) were titrated as above until the phenolphthalein absorption band became just perceptible when 0.5 inch (1.26 cm.) of the solution was viewed through the hand spectroscope. The amount of alkali added was assumed to be not more than 0.1 cc. in excess. The flask was stoppered and allowed to stand overnight, so that the excess alkali would be taken up by the esters in the rosin. No absorption band was then visible through a layer of solution 0.5 to 1 inch (1.26 to 2.5 cm.) thick. However, on the addition of 0.1 cc. of alkali the absorption band reappeared in 1 inch (2.5 cm.) thickness.

The appearance of the absorption band is illustrated by the spectrograms in Figure 1 taken on a spectrograph of moderate dispersion, using a tungsten lamp as the source of light. The low dispersion of the hand spectroscope is more favorable for detecting the presence of the faint absorption band than a higher dispersion instrument, and in the visual method the band appears narrower and more distinct than in photographs. The spectra are for 0.5 inch (1.26 cm.) thickness of the B rosin solution containing phenolphthalein (1) with no free alkali present; (2) at the end point [band appears in 1-inch (2.5-cm.) layer but not 0.5-inch (1.26-cm.)]; (3) 0.1 cc. alkali in excess [band appears in 0.5-inch (1.26-cm.) layer]; (4) 0.2 cc. alkali in excess; (5) tungsten lamp; and (6) mercury arc.

The following procedure is proposed for determining the acid number of low-grade rosin:

Place 100 cc. of 95 per cent alcohol and 1 cc. of 1 per cent alcoholic solution of phenolphthalein in a 300-cc. Erlenmeyer flask. Add 0.5 *N* standard aqueous alkali solution until the absorption band appears in 1 inch (2.5 cm.) thickness. This requires about 0.05 cc. excess. Add 5 grams of sample, stopper, and allow the rosin to dissolve at room temperature. Add rapidly about 1 cc. less than the expected or theoretical quantity of 0.5 *N* alkali. After the addition of each successive 0.05 to 0.1 cc. of alkali, hold the flask in an inclined position towards a source of light, preferably daylight, and view 0.5 to 1 inch (1.26 to 2.5 cm.) of the solution through a hand spectroscope. The end point has been reached when the absorption band becomes just perceptible.

Typical results obtained on some low-grade rosins by this proposed method are shown in Table I.

Table I. Typical Results on Low-Grade Rosins

	Sample 1[a] FF wood	Sample 2[a] B gum	Sample 3 B gum	Sample 4 D gum	Sample 5 E gum
Individual determinations	151.6	161.5	156.0[a]	161.0[a]	157.2[a]
	151.3	161.5	156.3[a]	161.3[a]	157.2[a]
	151.6	161.2	156.0[b]	160.7[b]	156.8[b]
	151.0	161.2	155.8[c]	160.8[c]	157.1[c]
Average acid number	151.4	161.4	156.0	161.0	157.1

[a] Determinations made on 5-gram portions.
[b] Determinations made on 5.5-gram portions.
[c] Determinations made on 4.5-gram portions.

The probable error in titration by this method is not greater than 0.1 cc. of 0.5 N alkali, corresponding to an error of less than 0.6 in acid number when a 5-gram sample is used. This is equal to the accuracy ordinarily obtained in titrating a 1- to 2-gram sample of high-grade rosin by the conventional method. The acid number can therefore be reported to the first decimal place.

Summary

With the aid of a direct-vision hand spectroscope for observing the end point, the acid number of the lowest grade (reddest) rosin can be determined with a degree of accuracy equal to that ordinarily obtained with high-grade or yellow rosin.

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Quantitative Estimation of Furfural at 0° C. with Bromine

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The quantitative estimation of pentoses and pentosans is often required in the work of agricultural experiment stations, medical research laboratories, paper mills, and rayon and textile plants. The usual procedure involves the distillation of the material with hydrochloric acid to convert the pentose derivatives into furfural, which is then determined in the distillate. Among the best known reagents for this latter purpose are phloroglucinol, thiobarbituric acid, and dinitrophenylhydrazine used gravimetrically, and bromine or bromate used volumetrically. The amount of bromine taken up by the furfural has been estimated by electrometric titration by Pervier and Gortner (*5*), Kline and Acree (*3*), Magistad (*4*), and others, and with an excess of bromine and back-titration with potassium iodide and thiosulfate by van Eck (*1*), Powell and Whittaker (*6*), Kline and Acree (*3*), and others. The gravimetric methods, especially with thiobarbituric acid, require at least 24 hours and involve the usual difficulties in filtering and weighing. The present volumetric methods are more rapid but less accurate when performed at room temperature. This is due to the fact that the rapid consumption of one mole of bromine per mole of furfural is followed by the slow addition of a second mole of bromine at 20° to 30° C. The large temperature coefficient of the second reaction observed by Magistad (*4*) and the authors introduces considerable error when determinations are made at variable room temperatures. Furthermore, it is found that considerably more than two molecules of bromine react with furfural at 20° to 30° C. when the reaction time is prolonged. The authors have, therefore, carried out a series of experiments on the reaction of bromine and furfural at 0° C. to determine whether the reaction could be limited to the first rapid step at this low temperature.

Experimental

The furfural was extracted with alkali to remove acid and fractionated under reduced pressure. It had a boiling point of 161.6° C. at 760 mm. Freshly distilled furfural was sealed in small glass balloons holding about 1 gram, and weighed. They were placed under water in graduated flasks and crushed, the flask was filled to the mark with water, and samples were pipetted into special Erlenmeyer flasks containing 200 ml. of 3 per cent hydrochloric acid. The 3 per cent hydrochloric acid was used because it is rarely exceeded in the usual furfural distillates and liberates the bromine fully. The hydrochloric acid in 6 to 12 per cent concentrations (*3, 5, 6*) decomposes the added thiosulfate. As it is very difficult to prevent the escape of bromine when standard 0.1 N potassium bromate plus potassium bromide is added to acidified furfural in open vessels, ground-glass-stoppered Pyrex Erlenmeyer flasks were fitted with two side arms to hold measured volumes of 0.1 N potassium bromate plus potassium bromide and of 10 per cent potassium iodide solution. To prevent accidental tilting and mixing, lead horseshoes were placed around the bottoms of the flasks, which were suspended from the edge of the ice bath with heavy wires fastened about the necks. The flasks were cooled between 0° and 2° C. in an ice and water bath and the reaction started by tilting the flask to allow the bromate solution to run into the furfural. The solutions were mixed and allowed to stand until it was desired to stop the reaction, when 10 ml. of 10 per cent potassium iodide in the other side arm was run into the mixture. The flask was removed from the ice bath and shaken vigorously to allow the enclosed bromine gas to react with the potassium iodide. The stopper was removed, rinsed as usual, and the contents were titrated with 0.1 N thiosulfate by using starch indicator. Under the appropriate conditions one mole of furfural reacts with one mole of bromine; hence one ml. of 0.1 N thiosulfate or 0.1 N potassium bromate is equivalent to 0.0048 gram of furfural.

Table I. Reaction of Bromine with Furfural at 0° C

Reaction Time	Per Cent of Theoretical Amount of Furfural Found: 100-mg. sample	57-mg. sample	45-mg. sample	10-mg. sample[a]
Min.	%	%	%	%
10 sec. (approx.)	...	...	31.5	...
1 (approx.)	...	...	99.3	...
2	...	...	100.1	99.1
3	...	100.0	100.2	100.0
	...	99.9	100.0	100.9
	...	99.7	...	...
4	...	...	...	100.5
5	99.6	99.8	100.3	...
	99.5	...	...	...
6	100.0	...	...	...
7	100.2	...	...	99.5
	100.3	...	...	...
8	100.1	...	...	...
	100.1	...	...	...
10	100.4	100.3	100.5	100.5
	...	100.1	...	...
30	101.3	101.8	102.0	101.4
60	103.0	103.0	103.4	102.5
90	...	105.5	...	...
240	...	...	112.5	...

[a] With small samples which use up only 2 ml. the titration error is necessarily large. 0.5 drop, or 0.02 ml. represents 1 per cent. This accounts for the larger variations in the percentages.

In the experiments given in Table I, 25 ml. of 0.1 N potassium bromate containing 50 grams of potassium bromide per liter were used. This quantity of potassium bromate is suitable for samples containing from 10 to 100 mg. of furfural. The results show clearly that at 0° C. and within about 3 to 10 minutes only one mole of bromine reacts with the furfural.

The use of specially constructed Erlenmeyer flasks eliminates the loss of bromine during the reaction. This is shown by the fact that the blanks run on the reagents standing as long as one hour checked within 0.1 per cent. As a further precaution against the loss of bromine it is advisable to seal the ground-glass joint with sirupy phosphoric acid.

The presence of direct sunlight should be avoided during the reaction, but no evidence of marked photochemical influence was observed under laboratory conditions in check experiments run in diffused light or in the absence of light.

Comparative studies at 0°, 5°, 10°, 21° C., and higher on both furfural and furoic acid indicate that the end point can be more quickly and accurately ascertained for the reaction of furfural with one molecule of bromine at 0° C. than with two molecules at higher temperatures. As furoic acid reacts very rapidly with more than one molecule of bromine under these conditions, it is suggested that furfural is converted first into a bromo derivative such as 4,5-dibromo-2-furfural (*2*).

Conclusion

A method is given for the quantitative estimation of furfural by treating it 5 minutes at 0° C. with an excess of 0.1 N potassium bromate plus potassium bromide in 3 per cent hydrochloric acid and determining the unused bromine with potassium iodide and 0.1 N thiosulfate. The furfural combines with one mole of bromine.

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A Study of Synthetic Cryolite Analysis

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THE chief distinction between natural cryolite (Kryolith) and synthetic cryolite lies in the fact that all the constituents of the natural variety are combined in a definite chemical ratio and that this salt always occurs as an individual and never as a mixture. Therefore, in order to determine its purity it is necessary only to make a single determination of any one constituent. On the other hand, synthetic cryolite usually contains other compounds such as sodium fluoride, aluminum fluoride, and occasionally aluminum oxide, which may vary over a wide range, depending to a great extent upon the method of preparation.

In view of the great differences which exist between these two products, an analytical procedure for the determination of each component in synthetic cryolite becomes highly desirable. The primary purpose of this investigation, however, has not been to set forth any definite analytical procedure, but rather to point out the differences between the two products, to identify some of the chief components, and to test the applicability of certain procedures which may ultimately lead to an acceptable method of analysis.

Solubility in Aqueous Solutions of Sodium Fluoride

As a basis for a possible quantitative estimation of sodium fluoride, the solubility of cryolite in aqueous solutions of this salt was determined.

Samples of natural cryolite to which were added known varied amounts of sodium fluoride were made up to a definite volume, stoppered tightly, and allowed to remain at room temperature (approximately 25° C.) for one week. Approximately a tenfold excess of cryolite was used to insure saturation. The flasks were shaken at frequent intervals in order that equilibrium might be established as completely as possible. At the end of this period, filtered portions of each solution were treated with about 10 ml. of perchloric acid and the fluorine was expelled by evaporating to fumes in a platinum dish. The aluminum in the residues was determined by means of 8-hydroxyquinoline and from the amount found the solubility of cryolite at the various sodium fluoride concentrations was calculated. The results of these experiments are given in Table I.

Table I. Solubility of Natural Cryolite in Aqueous Solutions of Sodium Fluoride

NaF Added	Na_3AlF_6 Found	NaF Added	Na_3AlF_6 Found
Gram/100 ml.	*Gram/100 ml.*	*Gram/100 ml.*	*Gram/100 ml.*
0.0	0.0345	0.035	0.0020
0.005	0.0263	0.050	0.0011
0.015	0.0176	0.075	0.0000
0.025	0.0059	0.100	0.0000

Determination of Sodium Fluoride

The possibility of a procedure for the direct estimation of sodium fluoride seems rather remote, owing to the lack of a suitable solvent in which sodium fluoride is alone soluble. As a result, an indirect procedure based on the insolubility of cryolite in the presence of sodium fluoride has been developed, which succeeds only in the absence of soluble or reactable aluminum salts. Since aluminum fluoride is completely insoluble, its presence causes no interference.

Procedure. Weigh out 5 grams of the sample and transfer to a 500-ml. volumetric flask. Add about 250 ml. of water and agitate vigorously for about 0.5 hour to insure complete solution of the sodium fluoride. Add a sufficient quantity of a known solution of sodium fluoride to give this salt a concentration of about 0.10 gram per 100 ml. Make up to volume, mix thoroughly by shaking, and filter on a dry funnel. Transfer 100 ml. of the solution to a 250-ml. beaker and make exactly neutral to phenolphthalein. Add a few drops of methyl red and titrate with a standard solution of yttrium nitrate. The sodium fluoride added subtracted from that found represents the amount present in the original sample.

In order to ascertain the applicability of such a procedure, synthetic mixtures were prepared from pure materials and the sodium fluoride was determined. The fluorine was determined by means of yttrium nitrate as outlined by the author (*3*) in a previous article. The results of these experiments are given in Table II.

Table II. Determination of Sodium Fluoride in Synthetic Mixtures

Na_3AlF_6 Added	Al_2F_6 Added	NaF Added	NaF Found
%	%	%	%
98.0	1.0	1.0	1.02
94.0	5.0	1.0	1.02
89.0	10.0	1.0	0.93
94.0	1.0	5.0	5.04
89.0	1.0	10.0	9.96
90.0	5.0	5.0	4.94
80.0	10.0	10.0	10.05

Determination of Sodium

The procedure outlined by Barber and Kolthoff (*1*), employing the use of uranyl zinc acetate as a reagent, has been found to be satisfactory for the determination of sodium.

Solution of Sample. Weigh out a 1-gram sample and transfer to a platinum dish. Add 8 to 10 ml. of a 30 per cent solution of perchloric acid. A few milliliters of nitric acid aid in the decomposition. Place upon the hot plate and digest at a low heat at first in order to prevent any loss due to spattering. Gradually increase the heat and, finally, fume to dryness. Moisten the residue with a few milliliters more of perchloric acid and again take to dryness. Repeat this operation at least three times. Add a small amount of water and digest on the hot plate until the residue has loosened from the dish. Transfer to a beaker, add about 25 ml. of hydrochloric acid, and heat until all salts are dissolved. Transfer to a 500-ml. volumetric flask, cool, make up to volume, and mix thoroughly by shaking. Transfer 10 ml. of the solution to a 100-ml. beaker and evaporate until it just begins to crystallize. Add a few drops of water to dissolve any crystals and precipitate the sodium according to the procedure of Barber and Kolthoff (*1*).

Table III. Determination of Sodium in Natural Cryolite

Sodium Present	Sodium Found: $HClO_4$ decomposition	Sodium Found: $HClO_4 + B_2O_3$ decomposition	Sodium Found: H_2SO_4 decomposition
%	%	%	%
32.86	32.85	32.57	32.56
32.86	32.85	32.53	32.55
32.86	32.84	32.49	32.52
32.86	32.84	32.47	32.51
32.86	32.84	32.45	32.50

Sulfuric acid, perchloric acid, and perchloric-boric acid mixture (*4*) were used for decomposing the cryolite. The decomposition was carried out in a platinum dish, with the exception of the perchloric-boric acid mixture which was done in a Pyrex beaker. Although good results were obtained by all three methods, those obtained with the perchloric acid decomposition were considerably better and are to be preferred.

The acidity of the solution from which the sodium was precipitated seemed to be of no great importance as long as there was sufficient acid present to hold the alumina in solution. As much as 1 ml. of concentrated hydrochloric acid and as little as 1 ml. of 0.5 *N* hydrochloric acid was used with equally good results.

It was found necessary to use an improvised water bath when precipitating the sodium, so that the temperature of the solution at the time of filtration was approximately the same as that of the reagent when filtered from the triple salt. The wash solutions should also be of the same temperature.

Natural cryolite obtained from Greenland was used for the experiments. The material was selected very carefully by hand and analysis showed no trace of impurities. The results of these experiments are given in Table III.

Determination of Moisture

The determination of moisture in synthetic cryolite may be accomplished with fair success, providing certain precautionary measures are taken. The water content usually varies over a wide range and is always bound rather firmly. Heating cryolite at relatively high temperatures in the presence of water results in partial hydrolysis with the formation of alumina and the liberation of fluorine as hydrofluoric acid. The volatility increases rapidly with an increase in impurities. For further details, the observations of Fredotieff and Iljinsky (*2*) on the system sodium fluoride–aluminum fluoride may be consulted.

In general, it was found that synthetic cryolite could be dried satisfactorily to constant weight at a temperature of 700° C. Practically no change in weight was observed after igniting for 1 hour, though occasionally a sample was found which decomposed at this temperature. However, there are no means by which such a sample may be identified beforehand; this can be done only by trial. At 800° C. practically all synthetic cryolites investigated showed considerable decomposition.

A number of samples of synthetic cryolite, which are fairly representative of the product now on the market, have been analyzed according to the above outlined procedures. The total fluorine was determined as outlined by the author (*3*), and the alumina, by means of 8-hydroxyquinoline after expelling the fluorine.

As will be seen, samples 5, 6, and 7 contain rather high percentages of free aluminum oxide. The fluorine found in samples 8, 9, and 10 is in excess of that required for the compounds which are most commonly present in synthetic cryolite. This would seem to indicate the presence of other fluorine compounds which are perhaps of a more volatile nature. The fact that sample 8 slowly decomposed at 700° C. substantiates this belief to a certain degree. Since only a limited quantity of these samples was available, a further and more complete investigation could not be made.

Table IV. Analysis of Synthetic Cryolite

Sample	Na	F_2	Al_2O_3	Na_3AlF_6	NaF	Al_2F_6	Excess Al_2O_3	Excess F_2	H_2O	Total
	%	%	%	%	%	%	%	%	%	%
1	32.34	53.78	24.19	97.69	0.45	0.81	0.0	0.0	1.03	99.98
2	31.36	52.51	23.79	92.82	1.56	2.09	0.0	0.0	2.74	99.21
3	31.65	52.56	23.52	91.32	3.00	2.24	0.0	0.0	3.20	99.76
4	32.49	52.51	22.64	87.40	6.88	2.37	0.0	0.0	2.22	98.87
5	30.41	52.04	25.06	81.89	6.40	5.42	1.91	0.0	4.72	100.34
6	24.30	48.48	30.60	72.79	0.70	12.67	5.35	0.0	N. D.[c]	91.51
7	16.99	31.22	42.00	46.38	3.20	9.95	24.72	0.0	15.94	100.19
8[a]	28.73	53.78	24.10	84.84	1.56	5.80	0.0	3.07	5.38	100.65
9[b]	27.79	51.26	24.53	77.29	4.37	9.53	0.0	0.85	4.45	96.49
10[b]	27.00	51.29	24.90	74.34	4.69	11.31	0.0	1.14	5.23	96.71

[a] Decomposed slowly at 700° C.
[b] Ignited at 500° C.
[c] N. D. Not determined.

The basis for the calculations is as follows: The amount of sodium combined as free sodium fluoride, deducted from the total sodium, represents the cryolite content and the remaining fluorine and aluminum are calculated to aluminum fluoride, aluminum oxide, or excess fluorine as the figures permit. The results of these analyses are shown in Table IV.

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Methods for the Control of Lubricating Greases

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In recent years much thought has been given to the development of new testing apparatus and to the improvement of methods for the proper classification of lubricants. The results of so-called standard tests do not always agree with those obtained under service conditions, chiefly because the test may measure an entirely different property from that which is involved when the lubricant is functioning in service. This is especially true with regard to greases.

This paper briefly describes a number of new test methods and instruments devised specifically for the determination of those characteristics of greases not readily obtainable by standard laboratory methods.

Lubrication engineers agree closely in their selection of oils for use in various types of machines, but frequently disagree in their recommendations of greases to meet certain requirements. Ordinarily the most important property of a lubricating oil is its viscosity, although sometimes such other characteristics as carbon residue and pour point of motor oils, demulsibility of turbine oils, stability, etc., may also be of considerable significance. With greases the matter becomes more complicated, since the Saybolt Universal viscometer gives fictitious readings even on light fluid greases and cannot be used at all on heavier greases. In general, consistency (or firmness) of a plastic grease is its most important property, although the kind and amount of soap content, the viscosity of the mineral oil, and the dropping point of the product are also sometimes very important.

Oils and greases should be tested at temperatures comparable with service conditions and the instruments employed most not only read accurately at those temperatures, but also furnish useful information as to the important properties of the lubricants.

Viscosity

The Saybolt Universal viscometer, which is the standard instrument for oils in this country, may be employed satisfactorily over a fairly wide range for oils, but should not be used for testing even the light summer grades of greases.

Lubricating oils follow the law of viscous flow: that rate of flow through a capillary is proportional to the total force producing the flow. Greases and other plastic materials do not follow this law, however, but require a definite initial pressure before any deformation takes place. Under the high shear rates met with in bearings or in gear cases, for example, greases have definite apparent viscosities; but under the very low rates of shear occurring in the Saybolt instrument the reading may vary from several times the apparent viscosity to infinity, depending upon the grade and kind of grease under observation. The Saybolt-Furol orifice (about 0.125 inch in diameter) or one 0.25 inch in diameter may be used with greater accuracy than the Universal for semi-fluid greases, such as gear lubricants, etc. The viscosity of plastic greases is conveniently and more accurately determined by means of a pressure viscometer.

Many laboratories make a great mistake, therefore, in using the Universal viscometer for greases. Furthermore, a viscosity reading at 210° F. usually does not indicate what the viscosity might be at 100° F., for example, because of a change in the grease structure with increase of temperature.

For the purpose of calibrating pressure viscometers and other instruments, and for use in the development of a new viscosity-temperature chart, several years ago this laboratory made a very careful comparison of the Saybolt Universal with the Furol orifice and with two other orifices (0.188 and 0.25 inch in diameter).

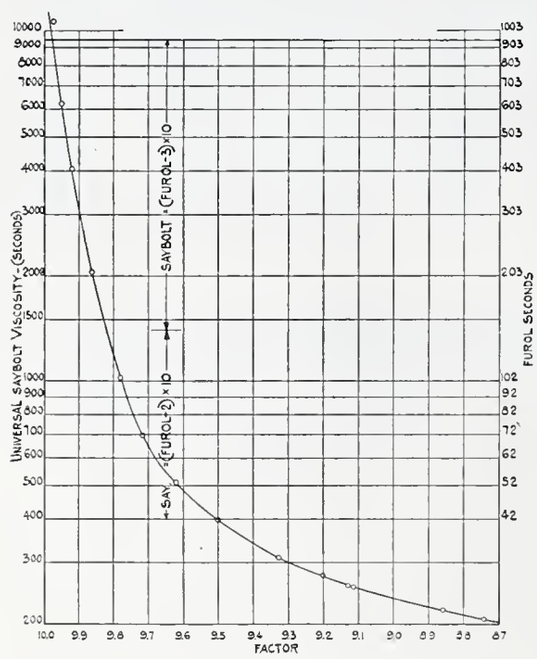

Figure 1. Relation of Saybolt Universal to Furol Viscosity

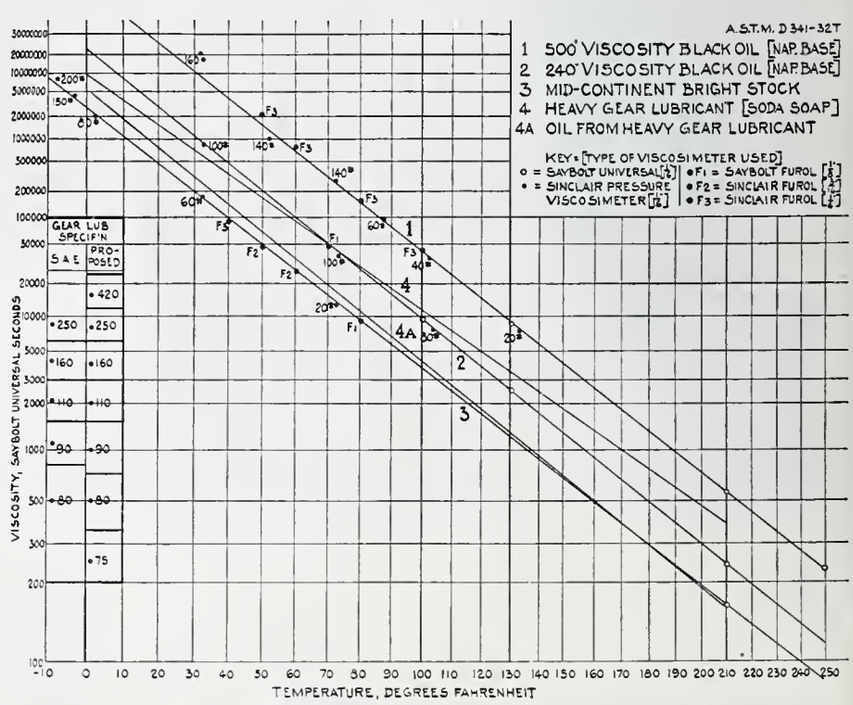

Figure 2. Viscosity Readings of Various Lubricants as Determined by Different Methods

Figure 1 shows the relation between a Saybolt Universal and a Furol orifice, both instruments having been checked previously by the Bureau of Standards. Each of the fourteen points on the curve is the average of from three to six check readings in both instruments. It can readily be seen how much error is occasioned by the use of 10 as a factor. Existing charts are inconvenient, inaccurate, and do not give data above 1000 Saybolt seconds, just when the Furol becomes useful and the Saybolt Universal begins to be less convenient, if not less accurate. Figure 1 is not suitable for converting Furol readings to Saybolt seconds. The author has discovered a better method by which conversion may be made without the use of tables or curves.

Note the Furol readings appearing at the right-hand scale corresponding with their respective Saybolt readings at the left. Note that above 1400 Saybolt seconds (about 140 Furol) the rule is to subtract 3 from the last digit of the Furol reading, and to add a zero. Between 400 and 1400 Saybolt seconds (42 to 140 Furol seconds) 2 is subtracted and a zero annexed. This gives an accuracy of less than 0.1 per cent over the entire range, except in the transition area (1000 to 2000 Saybolt seconds) where the error still is less than 0.5 per cent. Furthermore, this rule is easily remembered, eliminates the necessity of all charts, and hence is more convenient and very much faster in operation. The 0.188- and 0.25-inch orifices (designated as F_2 and F_3) were also carefully checked against the Saybolt or Furol (F_1) as well as against each other. The F_2 and F_3 orifices were found to have factors of 39.0 and 93.15, respectively, which give Saybolt readings with an accuracy of 0.3 per cent when used within their proper ranges.

Figure 2 is a plot of four oils and a heavy gear lubricant in the manufacture of which one of the oils was used.

Note that Saybolt readings O, F_1, F_2, and F_3 all lie on the straight lines represented by the various products, as long as the rates of shear do not fall below certain minimum values. When the shear rate is too low, the reading is above the line. If two orifices of different diameters give the same converted Saybolt reading, both are reasonably sure to be correct and operating at proper shear rates. If they do not agree, the lower reading should be accepted as correct, unless a larger orifice later indicates a lower reading. This principle may be used with semi-fluid greases with fair results, but the pressure viscometer is by far the more convenient as well as accurate method to use. It is believed that the rate of shear for oils, using any of the above orifice instruments, should be between 0.01 and 1.0 ec. per second for best results. The use of the following orifices is recommended:

Saybolt for 40 to 3000 Saybolt seconds
F_1 for 3000 to 10,000 Saybolt seconds
F_3 for 10,000 to 500,000 Saybolt seconds

No definite information can be given for greases, for reasons stated above.

On Figure 2 note that the pressure viscosity readings are plotted 2° to 4° F. above the temperature of the test. This temperature difference is due to the work done on the lubricant in passing through the orifice, being 0° for light oils and 2° for heavy oils, and 2° to 4° for light and heavy greases, respectively. This gives apparent viscosities which are sufficiently accurate, provided the correct pressures are used, the minimum readings being plotted. On a 200-second black oil the author obtained 24 readings, with pressures ranging from 10 to 125 pounds, which averaged the same within an error of 0.6 per cent. Heavy greases like universal joint grease can be checked within an accuracy of 2 per cent, while lighter greases check as well as do oils in a Saybolt Universal viscometer.

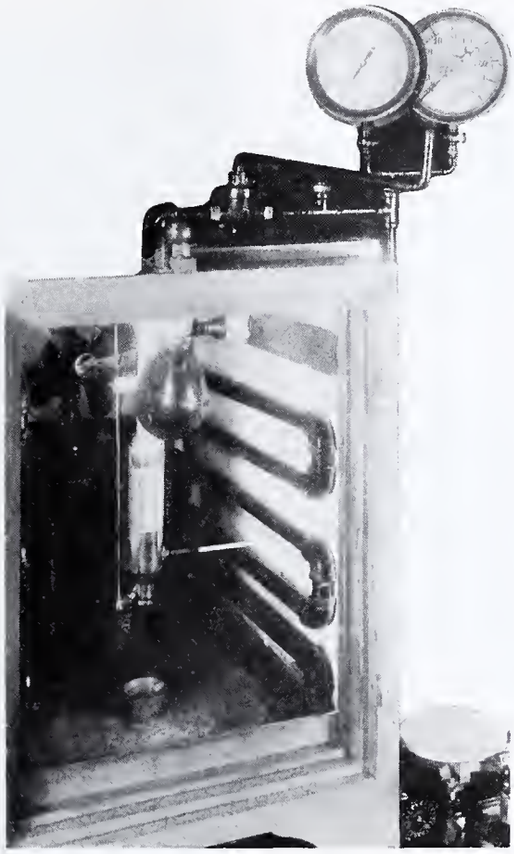

Figure 3. Sinclair Pressure Viscometer

The sleeve test and adherometer instruments (described below) make correct readings possible when the F_3 and pressure viscometer fail to give correct readings because of too low a shear rate.

In making the proper selection of a grease it is necessary to know the kind of grease best fitted for the specific service, the most satisfactory consistency for proper feeding and retention in housings, and the mineral oil which has the correct viscosity for that particular machine. Determining the kind and per cent of soap is of course the chemist's work, and is not discussed in this paper. The determination of the viscosity of the mineral oil contained in an unknown grease is not only expensive and laborious but the results are often in doubt, because of the presence of fatty acids which were saponified in the grease but in the separated oil are present in greater or less amounts, causing the viscosity readings to be in error. The author has separated oils from their greases by application of pressure and found viscosities of the separated oils to check satisfactorily with the original viscosity of the oil put in the grease. The question arises whether we want the viscosity of the mineral oil only, ignoring the effect of the soap, or whether we are really interested in the viscosity of the product as obtained by means of a pressure viscometer.

The author believes that the pressure viscometer is the proper instrument to use for the control of such semi-fluid products as gear lubricants. It has been used successfully at various Sinclair Refining Company laboratories for the past four years and is also valuable for the determination of apparent viscosities of heavy plastic greases.

The determination of the consistency of different kinds of greases is a subject which apparently has not received as detailed attention as other properties of oils and greases. Although the A. S. T. M. cone penetrometer seems satisfactory for medium grades of calcium and aluminum greases, experience in this laboratory indicates that it is unreliable and impracticable for fiber greases, especially those of extreme consistencies, such as light gear lubricants and heavy universal joint greases.

Pressure Viscosity

The urgent need of an instrument that will measure the viscosity of semi-fluid or plastic lubricants has been recognized by a number of experimenters for some time and various designs have been employed with encouraging results. The general arrangement and appearance of the Sinclair pressure viscometer is shown in the illustrations. A more recent development has an electric resistance-bulb thermometer, turntable for sample cups, and other improvements, yet in principle it is the same as the one illustrated in Figures 3 and 4.

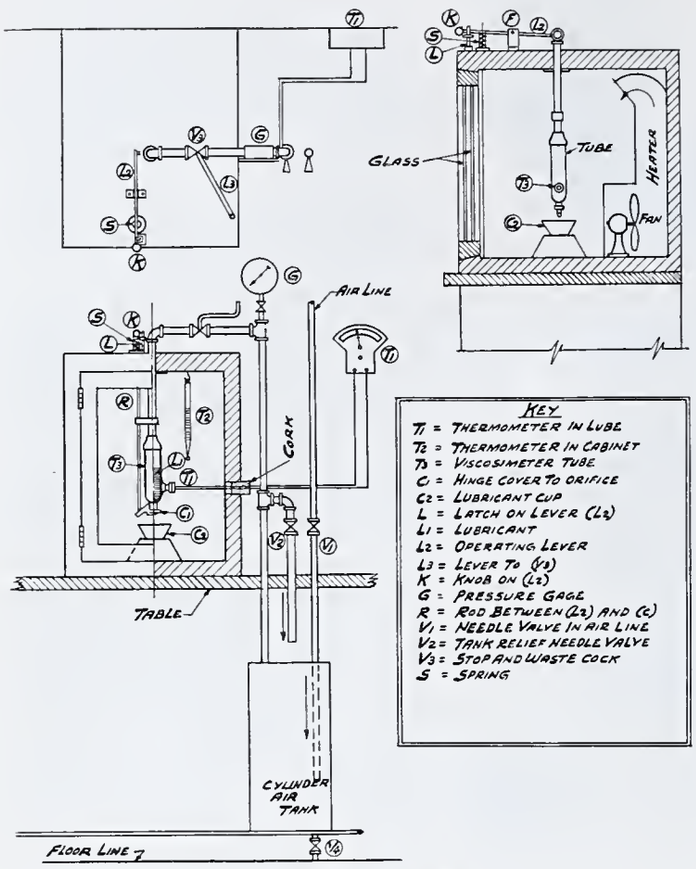

FIGURE 4. SINCLAIR PRESSURE VISCOMETER AND AUXILIARY EQUIPMENT

The tube is a nickel-plated steel cylinder (2 × 8 inches), the top cap of which is connected to a 0.75-inch pipe, communicating with a constant-pressure air tank. Accurate and convenient control of air pressure is accomplished by two needle valves, V_1 and V_2, or by automatic pressure regulator. The stop and waste valve V_3 enables one to apply pressure to the lubricant in the tube for any desired period of time or to cut off and instantaneously release the pressure within the tube, by throwing lever L_3 to the right.

The pressure is read on a calibrated gage, G. The cabinet is well insulated and provided with refrigeration and heating facilities, the efficiency of which greatly depends upon the circulating fan.

PROCEDURE

About 0.5 to 0.75 pound of the sample is placed in the tube, care being taken that there are no air pockets. The tube is screwed into place and cover lever connected. The thermometer is then screwed into place. The lubricant is brought to the desired temperature by proper manipulation of heating or cooling devices. "Overshooting" of the box temperature avoids much delay and should be practiced except when the sample is near the test temperature. To insure uniform temperature throughout the sample it is necessary to hold the sample and cabinet at the test temperature (± 0.2° F.) for at least 5 minutes, without noticeable change in the temperature of the sample, before applying the air pressure. Air from the pressure tank is applied without loss of time and adjusted to the correct value, an accurately calibrated gage being used. The pressure is maintained constant during the test, while the sample extruded into the cup is ordinarily about 50 grams. The time of efflux is the time that the lubricant is flowing, or from the time the orifice is uncovered until the pressure is released. The sample is weighed to the nearest tenth-gram and the pressure viscosity calculated by the formula developed by Parsons and Taylor:

$$PV = \frac{525 \times \text{seconds flowing} \times \text{pressure per square inch}}{\text{grams discharged}}$$

Usually two pressures are employed for known lubricants, but three or four pressures should be used on lubricants not run before. If the rates of shear in various tests are sufficiently high, the PV readings will check within 1 or 2 per cent, even though the pressures differ considerably. The minimum reading is taken as the correct value, which usually checks one or more other readings.

LOW-TEMPERATURE CONSISTENCY OF GEAR LUBRICANTS

The pour test of a motor oil is not a measure of its starting quality in low-temperature service, and at best is only roughly indicative of the temperature at which the oil fails to pass through the screen and into the circulating-oil pump. The pour test of a gear lubricant, likewise, is of very little value in determining whether the lubricant will feed satisfactorily to the ring-gear and pinion, or whether channeling will take place at 0° F., for example.

One gear lubricant with a 15° F. pour test may channel and fail to lubricate properly at 25° F., whereas another with a 25° F. pour may function satisfactorily at 0° F. Some lubricants—for example, those high in petrolatum or soap content—when allowed to remain undisturbed for a considerable period of time at low temperatures, will appear solid, but when agitated the consistency is greatly reduced although the temperature is practically unchanged.

Normally the lubricant in a rear-axle housing fills the tooth spaces and thoroughly coats the teeth submerged in the lubricant bath. Assuming that the temperature of the lubricant has dropped to 0° F. overnight, the torque, or drag, on starting, will depend upon the nature of the lubricant. Light-consistency lubricants generally offer only a small resistance to the passage of an object through them; others, though seemingly heavy in consistency, still permit relatively easy rotation of ring-gear; other lubricants cause excessively high starting torques.

After a few revolutions of the ring-gear, a certain amount of the lubricant, depending on the nature, will have been picked up by the ring-gear and carried to the pinion. Channeling will take place between the ring-gear face and the lubricant unless the lubricant is mobile enough to flow in and fill the gap. Again, the lubricant might flow in but refuse to adhere to the teeth, in which case the pinion will be lubricated only by the film originally left on the teeth, and for certain lubricants this film is insufficient for proper lubrication.

The performance of various lubricants can be studied satisfactorily by means of a rear-axle test set, provided with temperature control and a means

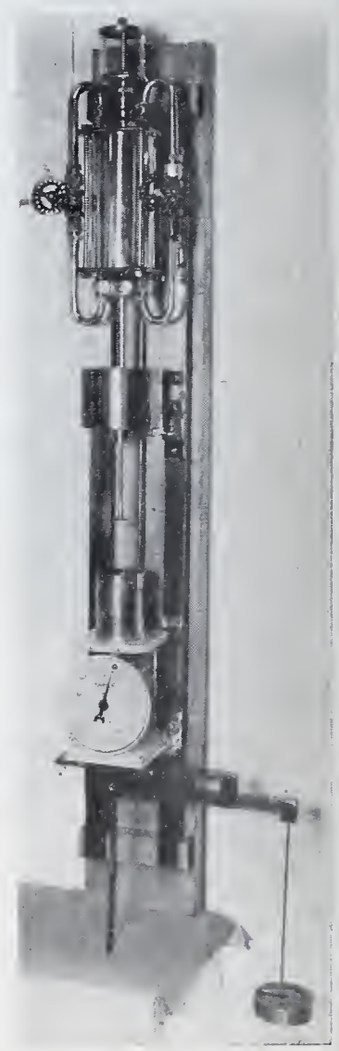

FIGURE 5. VISCIDOMETER (SPIKE APPARATUS)

for loading with normal operating tooth pressures. However, a much more accurate method has been developed, which expresses these various characteristics numerically and enables one to classify gear lubricants accurately.

Sinclair Viscidometer

The viscidometer was developed primarily to determine the viscidity of plastic or semi-fluid lubricants by measuring the resistance offered by the passage of an object through the body of the lubricant, which is indicative of the drag resistance, as well as the nonchannel characteristics of the product when employed as a rear-axle lubricant at low temperatures. It also measures the consistency of plastic lubricants at ordinary temperatures when a large plunger is used.

An added feature of this test throws further light on the non-channel property of a lubricant and indicates accurately the adhesiveness as related to the pick-up that may be expected on a ring-gear. Both viscosity and viscidity may be defined as the resistance offered by a fluid to the relative motion of its particles. This definition implies chiefly internal friction or cohesiveness. Orifice-type viscometers, like the Saybolt, measure viscosity in terms of both adhesiveness and cohesiveness, the former property being more pronounced the smaller the diameter and the longer the outlet tube of the instrument. The MacMichael, on the other hand, might be said to measure consistency or firmness, which is mostly a function of cohesiveness rather than adhesiveness. A gear lubricant, however, should also possess a certain amount of adhesiveness or the bob will not take hold, resulting in an erroneous reading.

Viscidity may also be defined as the quality possessed by a heavy sticky product, of being viscid and having a ropy glutinous consistency; hence the name viscidometer given to the instrument. As the plunger used in this test resembles a 60-penny spike, the test is commonly called the spike test.

The essential parts of this device are: a cylinder, 10, of seamless tubing (1.300 inch bore) for holding the test lubricant thermally insulated by a dead-air space between it and a seamless brass jacket (2 inch diameter); the assembly is held and insulated by a wooden holder, 14, which rests on an accurate dial weighing scale, 13. A spike-shaped plunger with 0.5-inch diameter head and 0.25-inch shank, 11, is pushed, head on, into the cold lubricant by means of an impelling weight, the velocity of descent of which is controlled by the passage of light oil through a needle valve, 21, which regulates the flow of oil from below piston 16 to the upper end of the containing cylinder, 17. The velocity of descent is held constant for all tests, being arbitrarily chosen as 26.5 (26 to 27) seconds for a 4-inch travel of the spike. The riser bottle, 22, furnishes make-up oil to the cylinder when the piston-rod is withdrawn. The impelling force (about 35 pounds) is due to the combined mass of piston 16, rod, and weight 12, which force is weakened during the test by an amount equal to the resistance between the spike and the lubricant, or the upward force on spike 11, as indicated by the scale.

Compensating weights (not illustrated) of various denominations are placed on weight 12 to keep the net effective force constant, thus maintaining the standard velocity of descent. The lever, and weights, 26, counterbalance the combined mass of test jar 10 and holder 14, thus making it possible to read direct on the dial the viscidity of spike-test resistance in ounces.

The reamer (Figure 6) insures an exact outage of 1 inch in the test jar, 10, or a constant quantity (4.375 inches) of lubricant for all tests. The scale is read precisely at points 0.5 inch above and 0.5 inch below the mid-travel position, which is defined as 2.25 inches below the original level of the lubricant. These two reading stations, A and B, are announced by the sounding of a buzzer. The buzzer circuit is completed by a brass plate on weight 12 coming in contact with the U-shaped contactor, 40, carried on a rod mounted in roller bearings, the bottom end of the rod being attached at the end of lever 26. The vertical distance between the nut, 40, and the mid-travel position of the test jar remains fixed; hence the buzzer sounds at A and B, regardless of the amount of depression of the scale platform, which for the full scale readings amounts to about 1 inch or more.

The device therefore consists of a constant velocity of descent

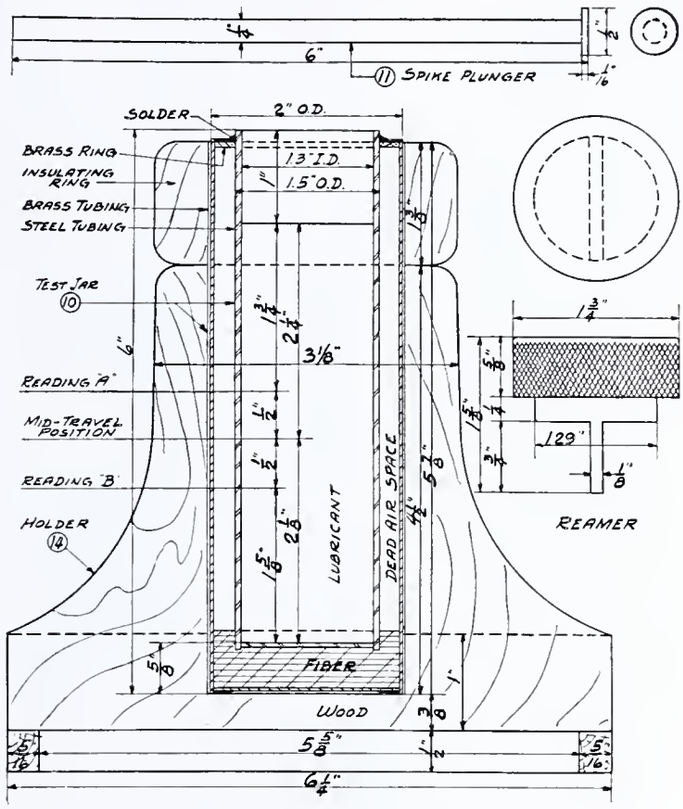

Figure 6. Viscidometer Jar and Holder

of a spike-shaped plunger; a well-insulated test jar, of accurate bore, for holding the test sample; and a means of counterbalancing the jar and holder so that the weighing device reads viscidity direct, at definite stations (A and B), 0.5 inch above and below the mid-travel position of the spike head. The viscidity is defined as the average resistance offered by the lubricant to the passage of the spike through it.

Procedure of Spike Test

A sample of test lubricant, at approximately room temperature, is placed in a spike-test jar to a depth of about 0.75 inch from the top and sealed with a cork stopper. Another jar is filled with the same sample or a similar lubricant, also at room temperature, into which a Redwood thermometer is inserted with its bulb near the middle of the sample.

The test jar and its dummy are now placed in a cooling cabinet with a breeze of air striking both jars similarly so as to insure the same rate of cooling. Other jars, containing similar lubricants of approximately the same consistency, may be cooled at the same time, the dummy indicating the temperature of all test jars. When the tests are to be made at 0° F., rapid cooling and satisfactory results are secured by holding the cabinet temperature at about −5° F. When the dummy reads 3° to 5° F. the cabinet temperature is brought to −1° F. and held there until the dummy reads exactly 0° F. The dummy is then held at 0° F. for 5 minutes, after which one of the test jars is placed in the holder, 14, and the wooden ring added, both the latter being also at 0° F. The spike is cooled to 0° F. and held until needed in an insulated billet (not shown) which was also cooled along with the jars and holder. The holder is placed on the scale platform and the pointer brought to zero by means of proper counterbalance weights, sliding poise, and dial adjustment. The cork is removed from the jar. The cold spike is now placed, as quickly as possible, in the chuck and the weight released by pulling the trigger, 25. Compensating weights are held in readiness and added to the descending weight, 12, equal to (or slightly greater than) the scale reading, until the spike reaches a point 0.25 inch above station A. A few ounces more or less than the A and B readings will not materially affect the rate of descent, inasmuch as each ounce represents only about 0.2 per cent of the total weight of 35 pounds.

The viscidity or spike-resistance of the lubricant is the average of the A and B readings or equivalent to the resistance at mid-travel position. As soon as the weight comes to rest, the spike is disconnected, gate valve 20 opened, and the weight raised to its top position, where it is held by catch 25.

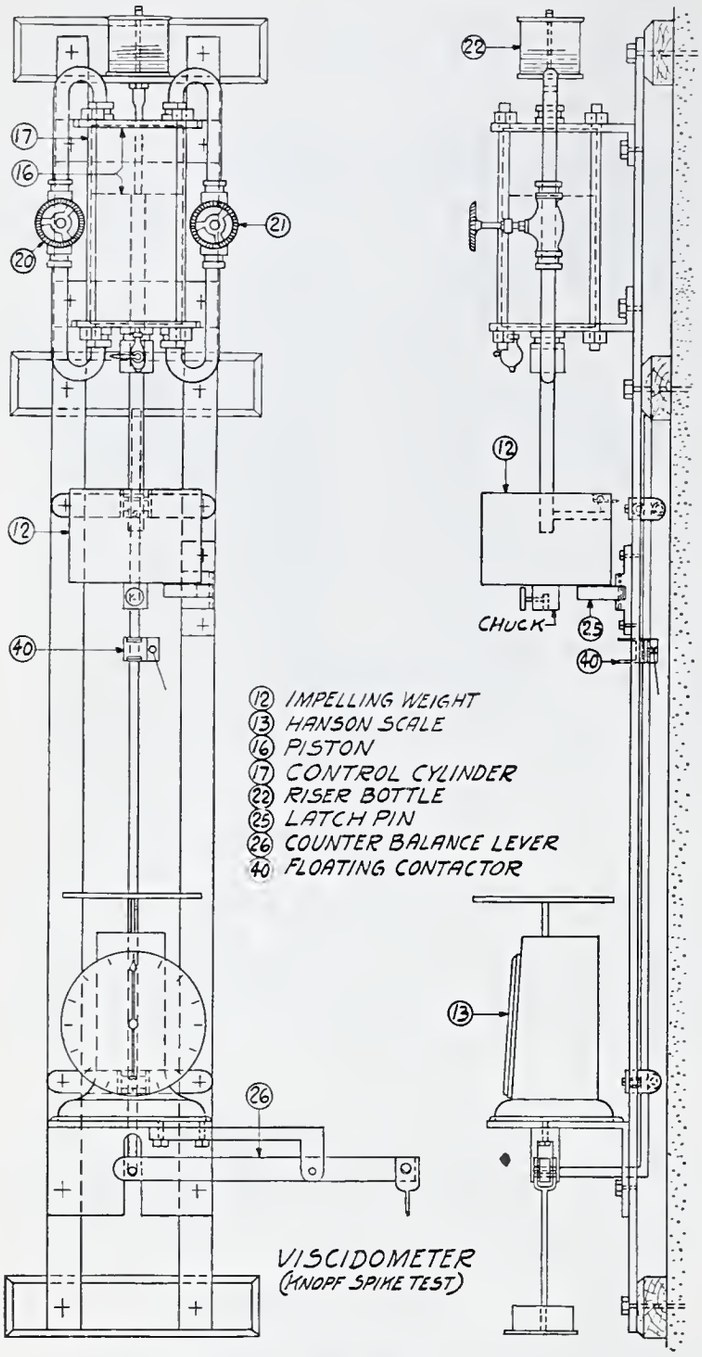

FIGURE 7. SPIKE-TEST MACHINE

Lubricants of considerable fluidity flow behind the head during the 60-second period, the amount being in proportion to the fluidity or nonchannel properties of the lubricant. On withdrawing the spike, the quantity adhering to it is noted, and the number of inches the lubricant strings out also observed. A combination of these two factors constitutes a basis for grading the lubricant as to its nonchannel and pick-up characteristics. Grade A means excellent, B is good, C is fair (tendency to channel and poor feeding), D is poor (with channel and practically no pick-up), while E is very poor. Petrolatum, for example, has an E grade with perfect channel and no pick-up at 0° F.

The resistance in ounces is something definite and can be checked within 2 to 5 per cent accuracy; the grading method, being based on judgment and correlation with gear-set tests, requires considerable experience and is difficult to describe accurately.

As we are measuring consistency, and therefore cohesiveness chiefly, we eliminate as much as possible all resistances due to adhesiveness by means of the large head and small shank of the plunger. With light winter lubricants there is sometimes a slight error due to the fact that the lubricant flows behind the head on the downstroke.

The viscidometer is invaluable as a control instrument in the manufacture of gear lubricants, as well as a means of comparing various products with regard to their low-temperature consistencies. When correlated with the rear-axle test, the results of the spike test enable one to predict accurately just how a certain lubricant will function at low temperatures. The spike test, however, does not give accurate information relative to its shifting resistance when employed in a transmission, being only fairly indicative of shifting ability. Another instrument very accurately measures this property.

The shifting resistance present in automobile transmissions in cold weather is due almost entirely to the adhesiveness of the lubricant in the clearance space between the sliding gear and the shaft on which it slides, and is also due, to a great extent, to the lubricant adhering to the tooth surfaces of the mating gears. In some designs the sliding gear is partly immersed in the lubricant bath, but the resistance from this source is relatively small as compared with those mentioned above.

Shifting resistance tests, in which a transmission is employed, are very inconvenient to run, and yield results which may not check within 20 or 25 per cent. The sleeve test was developed and used in this laboratory for some time to determine the relative adhesiveness of various lubricants. Although this device is more convenient and gives more consistent results than the shifting tests, it still falls short of being a practical control instrument. The sleeve test, or concentric cylinder viscometer, measures absolute viscosities of lubricants, with a range of 1500 to 100,000,000 Saybolt seconds. It has been found invaluable for the calibration of other viscosity instruments as well as for obtaining readings on heavy lubricants at very low temperatures when other instruments are difficult to manipulate. The author hopes in the near future to present a paper on this instrument.

THE ADHEROMETER

The adherometer is a device designed to simulate the sliding of a transmission gear on its shaft, except that in the instrument the shaft moves and the bore remains stationary, the relative motion being at about the same velocity as that of the sliding gear when hard shifting is experienced. Figure 8 gives a detailed drawing of the device, which may be described as follows:

A steel cylinder, 27, with a lapped bore of 0.628 inch (± 0.0002 inch), is provided with two thermometer wells, 29, which also act as air ducts in connection with vent passages 32 and 33 to allow air to escape from the lower end of the cylinder as the bullet is being pushed down by the spike plunger, 11, which is impelled by the same mechanism as in the spike test. The adherometer cylinder is thermally insulated by an air space between it and a brass jacket (2 inches in diameter), and by cork and fiber disks at the bottom. Six pins, 31, hold the cylinder concentrically in its jacket, and are rounded so as to cut heat conduction to a minimum.

The lubricating pin having a milled groove, 38, to hold the test lubricant is used to apply the lubricant to the bore of the cylinder. The bullet is 0.005 inch (± 0.0001 inch) smaller in diameter than the cylinder bore, leaving a 0.0025 inch clearance on each side. The sizing plug, 39, is 0.002 inch smaller than the bullet and like the bullet has spherical ends. The body of the lubricating pin is 0.002 inch smaller than the plug, 39. A slight excess of lubricant is deposited by the pin on the cylinder wall, but after the pin is withdrawn and the plug, 39, passed through the bore, only 0.001 inch of excess film is left on its walls. The magnet is employed for light lubricants to keep the bullet from slipping down of its own weight. The top end of the bullet for all tests is 0.375 inch down from the top of the cylinder, at a point fixed by the 0.625 inch thickness of the cork and the 1-inch magnet extension. The spike for the adherometer has a 0.437-inch head

to provide sufficient clearance for it to pass safely down the cylinder bore without touching. Its shank has notches cut at points 2.125 and 3.125 inches from the head end, which are the correct distances from the top of the bullet when at *A* and *B*. This is a gage for setting the contactors, 40, so that the buzzer will sound when the bullet is 0.5 inch above and 0.5 inch below the mid-travel position, which actually is 0.25 inch below the middle of the cylinder. As in the spike test, the two readings will be taken at *A* and *B* regardless of how much the holder, 14, and scale platform depress. Special holders are provided for cooling and holding the bullet and pin.

Adherometer Test Procedure

Corks are inserted in each end of the cylinder bore, extending inside about 0.25 inch. To reduce errors to a minimum the bullet starts from the same end, *T*, of the cylinder for all tests. The cylinder is placed in its jacket with end *T* down and the large cork left off to make cooling more rapid. A thermometer (reading to 0.2° F.) is inserted in the well. The cylinder, bullet, and lubricating pin are placed in a cooling cabinet which is held at 34° to 36° F., care being taken to see that no piece is allowed to cool as low as 32° F., for fear of moisture or frost deposit.

When the cylinder temperature has dropped below 40° F. (35° F. for light products) the thermometer is removed and the cylinder wrapped in a cloth to keep it cool. The corks are removed and the bore is lubricated thoroughly from both ends, care being taken to make the last pass with the sizing plug in the direction the bullet travels during the test. The previously coated bullet is now inserted in the *T* end, followed by a cork which holds the bullet 0.25 inch from the end of the cylinder and away from the vent. The cylinder is placed in its jar, bullet end down, and the other end is sealed by a small cork. The outfit is then placed in the cabinet and the thermometer inserted. Now the cylinder is cooled, with the cabinet held at −5° F., and when the temperature of the adherometer reaches −2° or −3° F. the thermometer and top cork are removed; the cylinder is inverted, bringing the bullet (end *T*) at the top. Then the jar and cylinder are placed in the cold wooden holder, 14, adding the wooden ring; the small cork is replaced by the large cork, which is forced down against the top end of the cylinder; the magnet is inserted and pushed down until the bullet reaches the proper starting point; and the thermometer is inserted. The temperature of the cylinder is brought to exactly 0° F. by several applications of the hand to brass jacket. The temperature is held at exactly 0° F. for 5 minutes or more, after which the thermometer and magnet are removed. The cylinder and holder (held by its base) are quickly carried to the spike-test machine. The dial is adjusted to 0° F. and the bullet pushed down by the small-headed spike. Compensating weights are added as in the other test to equal the amount of the scale reading at about 0.25 inch above station *A*. The large cork is not removed during the test.

The average of the *A* and *B* reading is taken as the adhesiveness or relative shifting ability of the lubricant if used in transmissions in cold weather. Winter lubricants are usually run at 0° F., whereas summer products are run at 20° F. The adherometer test enables one to classify lubricants with regard to shifting ability, and when correlated with actual transmission-shift tests furnishes valuable data. The author expects to be able to calibrate this instrument to read in Saybolt seconds.

The adherometer is convenient to operate and is accurate within 1 per cent. Furthermore, the results of a second and third passage of the bullet through the cylinder check with the first test, if the temperature is the same in all tests. Only one determination is usually necessary. The instrument besides measuring the shifting ability of gear lubricants, including those intended for steering gears, also gives information relative to the viscosity of motor oil at very low temperatures, classifying them as to their ability to start easily.

Consistency of Plastic Lubricants

The viscosity and nature of the mineral oil with which a gear lubricant is made, determine, to a great extent, whether the product will be satisfactory for winter, summer, or heavy-duty truck service.

The viscosity of plastic greases, which do not flow at all without the aid of pressure, can be determined only by the

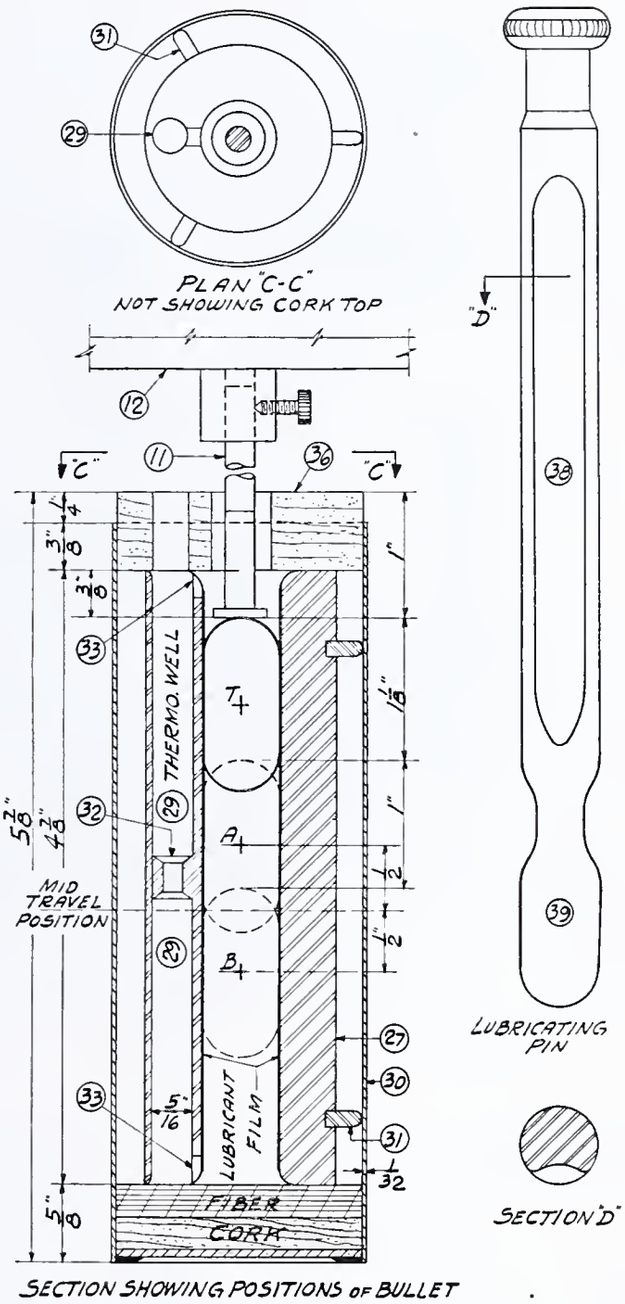

Figure 8. Adherometer

pressure viscometer. More pressure might be necessary, but the result will indicate very closely the viscosity of the mineral oil, being greater than the latter in proportion to the soap content.

In many cases the importance of the viscosity of a grease is only secondary to its consistency, which determines whether the grease will feed properly to the rubbing surfaces or resist being thrown out of housings, examples being wheel bearings of automobiles and universal joints, respectively. Often, if the consistency is correct, a grease will function satisfactorily even when the viscosity range is wide. Given a certain formula with definite viscosity of mineral oil specified, the most satisfactory control is by means of the disk-penetration consistency method, as follows:

Apparatus. Viscidometer (spike-test machine, Figure 5) with necessary counterbalance and compensating weights. A cabinet provided with heating and cooling facilities for bringing to and maintaining samples at desired test temperatures. The standard sample can is a straight-side tin can of internal diameter 3.188 inches and internal depth 3.75 inches with ring 0.562 inch from the top. A leather pad or support for holding two Saybolt thermometers in a vertical position, one at middle of can and the other

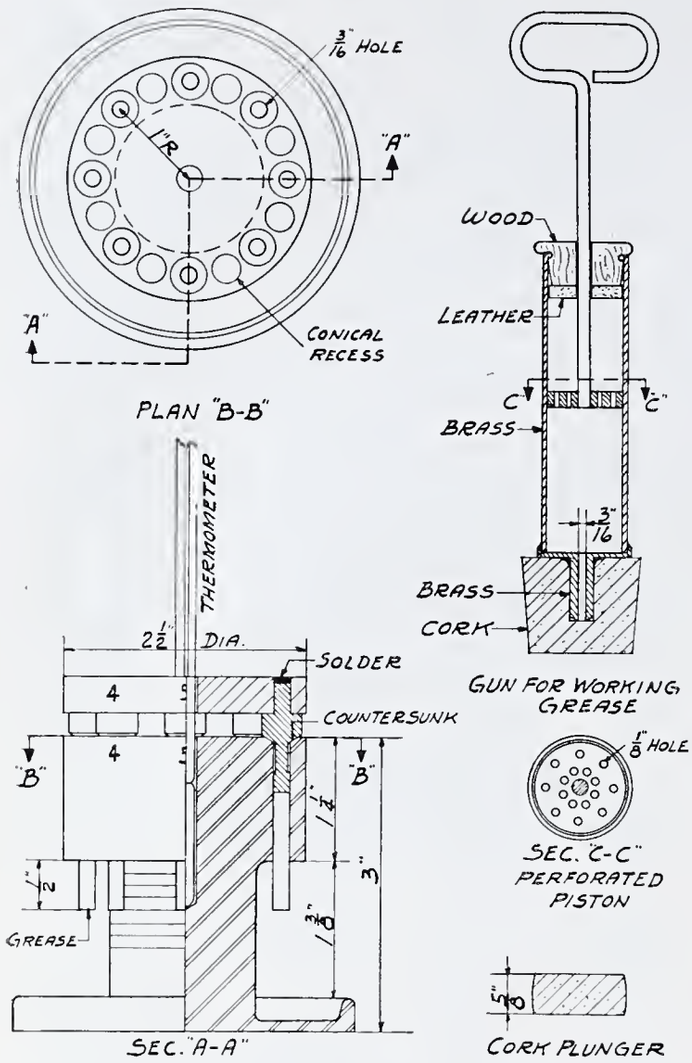

Figure 9. Drip Test Apparatus

about 0.5 inch from the side wall. A plate reamer for leveling surface at 0.562 inch outage. Stop watch or sand glass. Disk plunger head 1.3 inches diameter and 0.25 inch shank.

Procedure for Chassis Lubricant. The sample can is filled, being careful to eliminate air pockets as much as possible, which can be done by rapping the bottom of the can several times while filling, until the level does not lower with further rapping. The can is filled to about 0.375 inch from the top and the 70° Saybolt thermometers are inserted with bulbs just submerged, using the leather holder to support them in a vertical position.

The sample is placed in the cabinet and its temperature brought to 70° F. When both thermometers have stood for 5 minutes at 70° F. (± 0.2°), with the cabinet also at the same temperature the thermometers are removed, the can is rapped on the bottom, and the sample leveled off with the reamer, leaving a smooth surface 0.562 inch from the top of the can. This operation should not require more than half a minute. The can is now placed upon the scale, elevated 1.125 inches by means of the wooden block and in the middle of the platform. The scale hand is brought to the zero of the dial by means of the counterbalance weights. Assuming that the needle valve has been previously set so that the plunger will descend at the proper speed of 26.5 (26 to 27) seconds for a 4-inch travel, the weight is released. As the disk comes in contact with the sample the platform will sink, the amount depending upon the consistency of the grease. The scale hand moves very rapidly at first, but soon reaches a steady value. As quickly as possible compensating weights approximately equal to the scale reading are placed upon the impelling weight. The purpose of the compensation is to restore the original weight (about 35 pounds) of the moving parts, the net weight of which has been lowered by an amount equal to the upward pressure of the grease, or the dial reading at any instant.

Compensation will be close enough if within 50 grams of the dial readings, or 0.33 per cent error. Entire attention should be given to reading the scale about 1 or 2 seconds before the buzzer sounds, and to promote greater accuracy of the scale reading, the scale, or its base, should be rapped gently while reading the dial. The buzzer is set to sound at points A and B, which are 0.5 inch above and 0.5 inch below the middle of the sample, respectively. The two readings are averaged and converted to ounces, the conversion and correction for slight scale errors being accomplished in one operation. The corrected average resistance in ounces is known as the disk-penetration consistency.

Further information relative to the nature of the soap content and to the adhesiveness of the lubricant is given by a system of grading. Exactly one minute from the time the plunger touches the surface of the lubricant, the can is held in one hand while the plunger is withdrawn vertically along the center axis, noting the amount adhering to the plunger and the extent it strings out. An A grade indicates that the lubricant is semi-fluid and that not only did it close in behind the disk head on the down stroke, but that the material is also quite adhesive. These are desirable properties. E indicates a perfect channel, as is obtained with cup-greases. The down stroke of the plunger creates a well, the edge of which may be square, rounded, or partly rounded.

Down Stroke of Plunger. A calcium grease will produce a relatively sharp shoulder on the edge of the well made by the plunger, while a soda soap gives a rounded edge and a combination soap gives an intermediate condition (Table I). The round, half-round, and square shoulders may be designated as $A°$, A' and A'', respectively. To one accustomed to this test a designation such as PD at 70° F. = 6 A′ means that at 70° F. the disk-penetration consistency is 6 ounces (resistance), that the lubricant is semi-fluid and adhesive, and that the shoulder on the down stroke was partly rounded. The important properties of the grease are fully described by this designation, which is that of a chassis lubricant which will function properly in a Tryon shackle and will outlast gear lubricants so often employed for this purpose. Nondrip quality to some extent is also indicated.

The disk-penetration consistency is obtained on heavy products such as Universal joint grease in the same manner, except that the standard temperature in such tests is 100° F. (± 0.4°) on both thermometers.

Table I. Method of Grading Spike and PD Tests

Grade, Withdrawal of Plunger	Gear Lubricants Spike plunger	Plastic Lubricants Disk plunger
A	No channel, closes entirely, long string, adhesive	No channel, closes, semi-fluid, adhesive
B	Nearly closed	Light plastic
C	Slight channel	Slight channel
D	Medium channel	Semi-solid
E	Solid, perfect channel	Solid, perfect channel

The ordinary method of obtaining the consistency of railway driving journal greases is by means of the Dow penetrometer. The cambric needle used in this test frequently enters crevices and air pockets in the grease, and at other times it may hit hard spots. A new method is being developed which employs a bullet-headed plunger (0.25 inch in diameter and 1.18 inches long) the shank being relieved (0.188 inch in diameter) so that the bullet only produces the friction. The bullet is forced into a block of grease (3.25 × 3.25 × 2.75 inches high) and the resistance is read just after the bullet is completely submerged and again 1 inch below. The readings check very closely.

The fact that adhesiveness is practically eliminated with the specially designed plunger (spike or disk plunger) is of much importance if consistency alone is to be measured. Furthermore, in the author's opinion, the shear rate should be the same and constant throughout a test, for all lubricants, and the resistance offered by the grease should be the measure of consistency. As far as is known, all other instruments of similar nature measure adhesiveness to a greater or less ex-

tent, because of the various designs employed for plungers. Very few instruments maintain constant shear rates, whereas others employ impact forces, the results of which in the author's opinion are more or less misleading.

The disk-penetration provides a convenient and accurate means for obtaining the consistency of greases over a very wide range of values. The author believes the principle is correct, since resistance is measured by a force, with shear rates uniform.

Grease Drip Test

Considerable difficulty is usually experienced at greasing palaces with certain fluid lubricants which drip from shackles and other parts while cars are being greased, resulting in messy floors, runways, equipment, and even operators. It is proper to force a surplus of grease through at every bearing point, and the grease, unless excessive in amount, should hang down like a ribbon and adhere to the parts until the chassis is completely lubricated, after which the excess grease is wiped off.

The purpose of the drip test is to determine the ability of a chassis lubricant to hang suspended as a ribbon from a hot surface, simulating the condition mentioned above. This test should not be confused with the standard dropping point method, although the dropping point is involved.

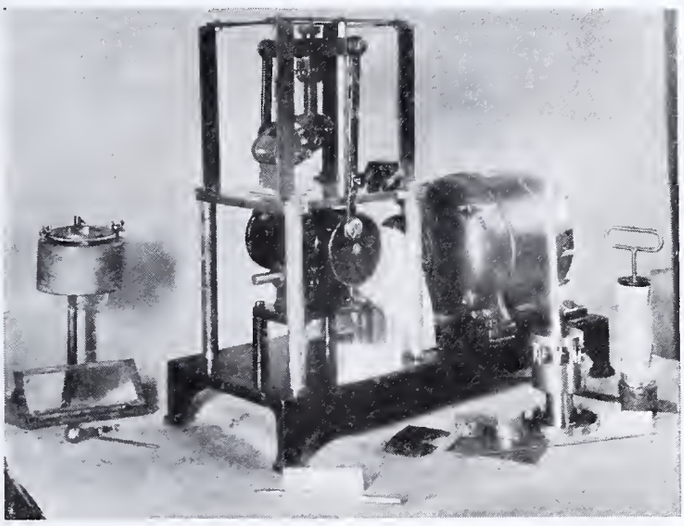

Figure 10. Drip Test and Shackle Test Apparatus

Apparatus. Figure 9 is self-explanatory, the right half of the sheet giving detailed drawings and the left showing the apparatus assembled for test. A grease gun for working the grease and for introducing samples in the test cylinders is also shown with other parts. The principal member is the cylindrical column with flanged base, like a huge collar button. There are eight equidistant vertical 0.188-inch holes drilled in the cylinder. A plate carrying eight 0.188-inch diameter pins permits the simultaneous introduction of all pins into holes, the purpose being to extrude exactly 0.5 inch of grease from all holes at the same instant.

Procedure. The base (or collar button), the pin plate, and grease gun filled with the test sample of grease are placed in a test cabinet and brought to 100° F. as read on a Saybolt thermometer inserted in the head. The grease is worked 20 double strokes, and the cork plunger is then inserted in the cylinder in front of the perforated piston, so that the grease can be expelled through the nozzle into the test holes.

The thermometer and pin plate are removed and grease is introduced into five or six of the holes, care being taken to see that each is completely filled with grease and free from air bubbles. It is advisable to extrude two or three times the amount necessary to fill each hole, the excess being struck off below the head and allowed to drop into the tray below. This striking off is done with one hand as the other is slowly operating the gun. About 0.125 inch of grease is allowed to project below the end of each hole. When five or six holes are thus filled, a leather wiper is used to shear each extruded portion off level after the countersunk part of the holes has been wiped clean. Thus all the holes contain exactly the same volume of grease.

The plate is placed on the head, the ends of the pins resting on the surface between holes and each pin adjacent to its corresponding hole. The thermometer is again inserted through the plate and into the "collar button." When the apparatus reaches 100° F. (± 0.2°) and remains constant for 5 minutes, the plate is turned so the pins will register with their respective holes. The plate should be lowered quickly (not dropped) and the stop watch started at the instant the pins reach their seats. This should extrude a column of grease 0.188 inch in diameter and exactly 0.50 inch long (a given volume for all tests). It can be seen that the grease is subjected to a tensile strength test, the weight of the grease tending to neck and pull apart just below the head. The chassis lubricant that will not drip at 100° F. from shackles while a car is being lubricated will also not drip from the collar button head in 15 minutes, the apparatus being held at 100° F. (± 0.2°) during the entire test. Even with care air bubbles sometimes enter the holes, breaking the grease column, which frequently causes the sample to fail. This condition is indicated by an elongation of 0.031 inch, or more, beyond the 0.5-inch mark within the first minute. All extrusions not exactly 0.5 inch long or those that are ragged should be eliminated by their removal. Four droplets should adhere for 15 minutes.

Shackle Test

Automobile shackles require an oil of considerable viscosity, inasmuch as the unit pressure is high. Oils with a small amount of asphaltic matter remain between the rubbing surfaces much better than do filtered oils, better lubricating the rubbing surfaces and eliminating wear and squeaks. The ordinary straight bolt or threaded shackle can be lubricated satisfactorily with oils or grease, provided the viscosity and nature of the oil are approximately correct. Shackles of the Tryon type, however, are much more difficult to lubricate, since a grease must be used which has the proper consistency, correct viscosity of oil, a certain degree of adhesiveness, and a soap or soaps of such nature that the lubricant will feed in the shackle at a given rate over a wide range of temperatures. Since the bearing surfaces in a Tryon shackle are relatively small and the unit pressures 3 to 5 times as great as in bolt shackles, a lubricant with EP (extreme pressure) quality is preferable to one of ordinary film strength.

Experimental samples of greases with various consistencies and types of soaps may be made and tested in a number of cars, equipped with Tryon shackles, filling the shackle tubes with an ordinary grease gun. All trace of excess lubricant is wiped off the shackle, leaving the outside perfectly clean. After the car has been driven 50 to 100 miles, inspection is made of the shackles. Each bearing point should show a drop or more of lubricant which has worked its way out of the cup, as proof that the lubricant is feeding. Inspection should be made after 500 miles and again at 1000 miles to determine how much lubricant still remains inside each tube. This is done by unscrewing the fitting and inserting a rod of diameter slightly smaller than the tube bore, forcing it into the tube until resistance is met. The distance that the rod enters the tube, compared with the total length of tube, indicates the percentage of lubricant that has worked out during the test. In this way one can determine the rate at which various lubricants feed at different temperatures. This is a very slow proeess, lacking accuracy and making it necessary to depend entirely upon the weather conditions, the driver, and the roughness of road he happens to traverse.

Procedure with Shackle Tester. Figure 10 illustrates a device which was developed for the purpose of oscillating a Tryon shackle in a manner simulating the condition of a car operating over a rough road.

A 0.33-horsepower induction motor, 1200 r. p. m., is connected to a speed reducer which translates the rotating motion to rectilinear by means of two pitmans, the speed of which is about 60 strokes per minute. A small pitman connects the cross-head to one side of the oscillating shackle bolt, the other bolt being

held rigid by a clamp. The small pitman has a hardened steel button which engages in a groove cut in one link of the shackle. At mid-position the button does not touch the link, whereas the cam action at both ends of the stroke causes the link to weave as it would on the road, because of the up and down motion of the springs.

Trays are set under the shackle to catch the grease which drips from each bearing point. The test is run for 12 hours and the amount of grease feeding out during the test noted. Some greases in a few hours will work out almost entirely, while others (like ordinary lime greases) will not feed at all.

A Tryon shackle on a Chevrolet car was filled with a pressure grease and driven for 10,000 miles without attention. In several hundred miles the shackle started to squeak and during the latter half of the test was very noisy. At the end of the test run, the shackle was completely worn out, yet three-fourths of the original charge of grease still remained.

This apparatus has the advantage over a car, inasmuch as the severity of weaving is controlled and maintained constant for all tests, many miles of travel being represented by the overnight run of 12 hours. Furthermore the outfit, being portable, can be placed in a cabinet held at any desired temperature, to furnish information on the feeding ability of various greases at different temperatures. This outfit is not used as a control test but to demonstrate the superiority of one type of chassis lubricant over others. Chassis lubricant production is also occasionally checked for feeding ability with this machine.

Conclusions

1. As viscosity is the most important property of an oil, it is essential that accurate determinations be insured by the use of suitable instruments and proper methods.

2. Employment of the A. S. T. M. viscosity-temperature chart (D-341-32 T) and the Sinclair Viscosity index is invaluable as an aid to the proper understanding of oils and greases.

3. More use should be made of the Saybolt-Furol instrument and larger orifices for the determination of heavy lubricants, especially those containing small amounts of soap. The pressure viscometer is convenient and accurate for the determination of the apparent viscosity of fluid, semi-fluid, and soft plastic lubricants and even universal joint greases; however, consistency for plastic products seems to be more important. The higher the viscosity of the mineral oil and the greater the soap content, the greater will be the pressure viscosity. Insufficient pressure gives too high a value. Minimum values, obtained at different temperatures, when plotted 3° high, fall on a straight viscosity line, representative of the lubricant.

4. In classifying greases, the consistency is usually more important than the viscosity of the mineral oil in the grease. As consistency is the internal resistance of a grease to deformation, methods should be used which measure this property only. The following items should be observed:

Deformation should be at a constant rate.

The resistive force offered by the grease to its displacement should be a measure of the consistency.

The cross-sectional area of the deforming tool (plunger) should be uniform, not conical or spherical.

The adhesive property of the lubricant should be eliminated by avoiding contact of the shank with the lubricant at the time the resisting force is measured. The spike test and disk plunger (PD) test described above comply with these requirements.

Very careful attention should be given to temperature. Control of 0.2° to 0.5° F. is possible.

5. True viscosity at low temperatures is very conveniently measured by means of the adherometer which gives data relative to the shifting ability of various gear lubricants.

6. Chassis lubricants should not drip, yet they should feed at a proper rate in Tryon shackles. The drip and shackle test outfits are a great aid in the production of suitable chassis lubricants.

The viscidometer has been in use for about 7 years and the pressure viscometer for 4 years at several laboratories of the Sinclair Refining Company and have insured satisfactory control. The author is continually attempting to make improvements in test methods whenever an opportunity presents itself and hopes that others will be inspired by this paper to develop similar methods along the same lines.

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Determination of Fluorides in Natural Waters

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THE wide publicity given to the findings of Kempf and McKay (*5*), Churchill (*2*), and Smith, Lantz, and Smith (*6*), in regard to the relationship between mottled tooth enamel and the fluoride content of drinking water, has resulted in extraordinary interest in the presence of fluorides in potable waters.

In April, 1933, the City of Los Angeles undertook, under the direction of H. A. Van Norman and R. F. Goudey, Bureau of Water Works and Supply, to determine the fluoride content of its sources of domestic water supply. This laboratory was then confronted with the necessity of adopting a suitable method for the quantitative determination of fluorine. After a thorough investigation of available procedures (*2*, *4*, *7*, *8*), a modification of the method proposed by Thompson and Taylor was found to be most reliable, convenient, and specially suited to routine determinations when a large number of samples are to be analyzed at any one time.

The method, as adapted to the determination of fluorides in natural waters, is as follows:

Reagents

Standard Sodium Fluoride Solution. Prepare a stock solution containing 2.21 grams of c. p. dry sodium fluoride per liter. Dilute 10 ml. of stock solution to 1 liter (1 ml. equals 0.01 mg. of fluorine).

Indicator. Prepare a stock solution as follows: (*a*) Dissolve 0.17 gram of alizarin sodium sulfonate in 100 ml. of distilled water. (*b*) Dissolve 0.87 gram of crystalline zirconium nitrate, c. p., in 100 ml. of distilled water.

Add (*a*) to (*b*) slowly with constant stirring. Shake at intervals and allow to stand overnight. Dilute 20 ml. of stock solution to 100 ml. to serve as indicator. When not in use, these solutions are best kept in a cool dark closet.

Hydrochloric acid, 3 *N*.

Sulfuric acid, 3 *N*.

Preparation of Standards

To each of a series of nine 250-ml. Erlenmeyer flasks, add 0, 2.5, 5.0, 7.5, 10, 15, 20, 25, and 30 ml. of standard fluoride solution (1 ml. equals 0.01 mg. of fluorine) made up to 100 cc. with distilled water.

The suggested standards cover from 0 to 3 p. p. m. of

fluorine, which is a suitable range for potable water. The fluoride content of the unknowns can be estimated to the nearest 0.1 p. p. m. by interpolation. These standards are treated in a manner identical to that prescribed for the unknowns below.

Procedure

A 100-ml. aliquot of the sample to be analyzed, freed from turbidity and suspended solids by filtration if necessary, is placed in a 250-ml. Erlenmeyer flask. To each 100-ml. aliquot thus measured, and to the prepared standards, add exactly 2.0 ml. of 3 *N* hydrochloric acid, 2.0 ml. of 3 *N* sulfuric acid, and 2.0 ml. of indicator solution.[1]

Place flasks on a hot plate. Bring the contents rapidly to the boiling point and remove soon after boiling begins. Do not allow to boil vigorously nor to simmer for a long time.

Four hours after cooling, or the following day, transfer the standards to properly labeled 100-ml. matched Nessler tubes and make up to the mark with distilled water. Transfer each of the unknowns, in turn, to a 100-ml. Nessler tube and compare its color with that of the standards.

If a reddish precipitate appears in any of the aliquots after cooling, disperse it by rapid whirling of the contents of the flask prior to their transfer to the Nessler tube and proceed with the determination as usual.

Discussion of Method

Thompson and Taylor, in their method for determining fluorides in sea water (*8*), recommend the preparation of fluorine standards with a solution of salts having a sulfate-to-chloride ratio analogous to that of sea water. The direct application of this procedure to fresh waters did not seem practical because the wide fluctuation of their chloride to sulfate ratio, as well as of the actual amounts of these radicals present, almost necessitates the preparation of a set of standards for each sample to be analyzed. This procedure, however, has been recently suggested, with some modifications, by Elvove (*3*).

The substitution of standards made up with distilled water for those prepared with a solution of the salts present in the unknowns did not prove successful when hydrochloric acid only was used for the acidification of samples and standards. Tests, made on a series of synthetic waters, indicated that the presence of sulfates interfered seriously with the quantitative determination of fluorides.

Attempts to remove the sulfates by precipitation with barium chloride, followed by filtration through asbestos, were not altogether satisfactory. However, the substitution of half the amount of hydrochloric acid, to be added to both the unknowns and standards, by an equivalent amount of sulfuric acid, effectively eliminated the interference of sulfates in the amounts normally found in fresh waters. Under these conditions it was necessary to increase the concentration of the indicator in order to obtain a color range, varying from pink to yellow-green, which would permit an easy matching of the standards with the unknowns.

The results of several hundred determinations, made with synthetic waters by the method here proposed, indicate that chlorides, sulfates, bicarbonates, sodium, calcium, and magnesium up to 500 p. p. m.; manganese up to 200 p. p. m.; silicates up to 50 p. p. m.; phosphates, boron, copper, and iron up to 5 p. p. m.; and sulfides up to 2 p. p. m. do not interfere with the quantitative determination of fluorine.

The permanency of the color allows the estimation to be made whenever convenient, within a day or so, after 4 hours following the heat treatment, provided that the samples and standards are treated at the same time and in an identical manner. Duplicate determinations on a number of samples have given results which agree within 0.2 p. p. m. In Table I, the fluoride recoveries obtained by the method here proposed from a series of natural waters are shown. The figures given are the average results of two sets of determinations made with the same waters on different days.

[1] The intensity and shade of the color produced depend on the concentration of indicator and of each of the acids in the aliquots. It is therefore necessary to add identical amounts of these reagents to both standards and unknowns in order to obtain the maximum possible accuracy in the determination. The use of narrow-bore 2-ml. pipets has been found satisfactory for the addition of acids and indicator.

Table I. Fluoride Recovery from Natural Waters by Modified Zirconium Nitrate–Alizarin Sodium Sulfonate Method

Laboratory No.	Description	Fluoride in Sample	Fluoride Added	Fluoride Recovered
		P. p. m.	*P. p. m.*	*P. p. m.*
287	Headworks line (infiltration gallery water)	0.4	1.0	1.4
297	Barnes City well	0.3	1.0	1.3
326	Marston's well	0.5	1.0	1.4
327	Owens River at Thompson's Ranch	0.4	1.0	1.3
328	Mammoth Creek (above lava)	0.2	1.0	1.1
329	Hot Creek at Co. Bridge	2.1	1.0	2.8
331	Owens River at Crooked Creek	1.2	1.0	2.2
333	Fish Slough	0.9	1.0	1.8
354	Lomita Well No. 5[a]	0.6	1.0	1.5
355	Wilmington Well No. 13[a]	0.6	1.0	1.4
403	Shaft No. 2 near Silver Lake[b]	0.3	1.0	1.2

[a] Slightly colored waters.
[b] Sample contained 1.5 p. p. m. hydrogen sulfide.

Organic matter and phosphates, if present in the samples in appreciable amounts, tend to throw some of the indicator out of solution. If the reddish precipitate formed is slight, it is possible to disperse it by rapid whirling of the contents of the flask and to compare the color as usual without difficulty or material sacrifice of accuracy. In extreme cases when the amount of precipitate is such that the matching of color cannot be made satisfactorily, the method proposed by Willard and Winter (*9*) or its modification as suggested by Boruff and Abbott (*1*) may be used to advantage.

Summary

The zirconium-alizarin method for the colorimetric determination of fluoride has been modified for the quantitative estimation of the ion in potable waters. The suggested procedure makes possible the use of distilled water in the preparation of the standards instead of synthetic water of similar mineral content as that of the water being analyzed. This permits the use of one set of standards for the determination of fluorides in any number of fresh water samples regardless of the composition of their mineral content. The method has been found to be reliable, convenient, and specially suited to routine determinations when a large number of samples is to be analyzed at any one time.

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Received November 3, 1933.

U. S. Exports of Scientific Instruments Decline. The value of scientific and professional instruments exported from the United States declined 15 per cent in 1933 compared with 1932, according to figures compiled in the Commerce Department. The totals for the two years were $3,710,662 and $4,406,527, respectively. Only two divisions of the professional instruments group recorded increases.

Action of Sodium Amide on Silicates and Refractories

P. Victor Peterson and F. W. Bergstrom, Stanford University, Calif.

A large variety of silicon-containing substances, including feldspar, bauxite, serpentine, soapstone, soda-lime and Pyrex glasses, burnt refractories, and clay, are completely decomposed by fused sodium amide. The aqueous solution of the fusion contains all of the silica as sodium silicate, and silicon may therefore be determined accurately by the usual methods of quantitative analysis. The optimum conditions for the fusions have been determined, and it is pointed out that the use of nickel crucibles eliminates the much more costly platinum crucibles necessary in fusions of silicate ores with sodium carbonate or hydroxide.

Sodium amide, as is well known from the work of Franklin (*5*) and his collaborators, is a base of the ammonia system, analogous not only structurally but also chemically to sodium hydroxide. It has frequently been observed that sodium amide is more reactive chemically than sodium hydroxide and a rather extensive literature has grown up in which many confirmations of this statement may be found (*1*).

The great reactivity of sodium amide, coupled with its relatively low melting point of 210° C., suggests that it may advantageously replace sodium hydroxide or carbonate in alkaline fusions designed to open up silicate ores or refractories prior to analysis. Furthermore, the use of sodium amide will permit the replacement of the expensive platinum crucibles required for the sodium hydroxide fusions with the much cheaper and fully as satisfactory ones constructed of nickel. It was with these considerations in mind that the present investigation was undertaken.[1]

Table I. Comparison of Analyses by Sodium Amide and Conventional Alkaline Fusion Methods

Name	Designation	Silicon Dioxide: Sodium amide method[a]	Silicon Dioxide: Alkaline fusion method[b]
		%	%
Ferrosilicon	B58[c]	75.4, 75.6[d]	75.6
Silicon	B57	96.9, 96.73[d]	96.8
Bauxite	B69	6.4, 6.44	6.32
Feldspar	B70	66.55, 66.59	66.66
Soda-lime glass	B80	73.9, 74.1	74.1
Glass sand	B81	99.3, 99.3	99.26
Lead-barium glass	B89	65.25, 65.39	65.4
Opal glass	B91	67.65, 67.65	67.6
Pyrex glass	..	80.2, 80.07	80.1
Burnt refractory	B76	54.7, 54.6	54.68
Burnt refractory	B77	32.34, 32.31	32.38
Czechoslovak clay	..	46.7, 46.6	46.9
Burnt refractory	B78	20.5, 20.63	20.69
Asbestine	..	61.1, 61.0	61.0
Calamine	..	29.0, 28.9	29.0
Serpentine	..	35.4, 35.1	35.2
Soapstone	..	40.2, 40.2	40.26
Feldspar	..	65.7, 65.5	65.6
Soapstone	..	36.5, 36.5	36.6

[a] Fused 2 to 3 hours at 330° C., a time usually longer than necessary (silicon and ferrosilicon, see Table III).
[b] Silicon and ferrosilicon were fused with Na_2O_2; the remainder with Na_2CO_3.
[c] Bureau of Standards standard analyzed sample No. 58, etc.
[d] Per cent of silicon element. Here and elsewhere, duplicate analyses of the same specimen are given.

Preparation of Sodium Amide

The sodium amide required in the present experimental work was prepared by a method that differs in slight detail from that already described by Dennis and Brown (*3*). Briefly, dry ammonia is passed through molten sodium at a temperature around 350° C. until complete conversion to amide has taken place.

The furnace used in the present investigation consists of a sheet monel metal can (5 inches in diameter, 6 inches high) around the circumference of which are spot-welded six 6-inch (300-watt) chromolox strip heating units, parallel to the axis of the cylindrical can. The number in operation at any one time is controlled by means of a tumbler switch which is placed underneath the transite board box that contains the asbestos insulation of the furnace. The current consumption can also be varied by a rheostat placed in the supply line. A heavy cover of monel metal (or nickel) is placed over the top of the furnace and the surrounding insulation. Through this cover passes an ammonia inlet tube, whose depth of immersion into the molten sodium is adjustable, a thermometer well, likewise long enough to dip into the melt, and an exit tube for ammonia gas, all made of nickel. Sodium is contained in a spacious nickel crucible placed within the monel metal can of the furnace.

After the conversion of the sodium to sodium amide by a stream of ammonia gas at 350° C., and after cooling, also in a current of ammonia, the crucible is placed mouth down in a large mortar, and the bottom and sides are tapped with a mallet until the sodium amide separates from the metal. The larger pieces are coarsely broken with a pestle, and rapidly transferred to bottles with tightly fitting ground stoppers, greased at the top. These bottles should contain an atmosphere of ammonia. (Sodium amide exposed to the atmosphere for any length of time should not be used because of the danger of explosion, *2*).

Experimental Method

The silicate mineral or refractory to be analyzed is thoroughly sampled and then ground until the desired degree of fineness is obtained, after which it is thoroughly dried at 110° to 140° C. Analysis should not as a rule be attempted on a sample which does not pass through a 200-mesh screen. The rather tedious reduction of the sample to this state of division is circumvented by the use of a mechanical grinding device.

The fusion is carried out in 100-cc. nickel crucibles, with the use of approximately 20 grams of sodium amide and 0.5 gram of the silicate ore. Half of the sodium amide is first placed in the empty crucible, and the specimen for analysis is spread over its surface and then covered with the remainder of the amide. The 100-cc. crucible is placed within one of 150 cc. capacity to guard against the loss of material by the creeping of the fusion over the sides of the containing vessel. The two crucibles, together with a number of other similarly arranged pairs, are then introduced into an electrically heated muffle furnace, previously heated to the temperature at which the fusion is to occur (Table II). A stream of ammonia gas is passed through during the fusion and the subsequent cooling of the melts to room temperature. Crucibles are removed from the furnace at definite intervals and the contents analyzed, if it is desired to determine the minimum time necessary for complete decomposition of the ore. At a temperature of 330° C., this time is generally about 20 to 30 minutes, although it is usually advisable to continue the fusion for an additional period to be certain of complete decomposition. Material of unknown behavior should be heated for 2 to 3 hours at 330° C.

[1] The methods of analysis described in the present article have been successfully used at the San Jose State Teachers College for a number of years.

Table II. Influence of Time, Temperature, Amount of Sodium Amide, and Size of Particles on Rate of Decomposition of Silicates and Refractories

Time of Heating[a]	Weight of Sample	Undissolved	
Min.	*Gram*	*Gram*	*%*
Feldspar, 200 mesh and finer			
Fusing temperature, 330° C.; amount of $NaNH_2$, 5 grams			
5[b]	0.5026	0.2737	54.3
7.5	0.5011	0.0438	8.7
10	0.4997	0.0294	5.9
15	0.5028	0.0180	3.6
25	0.5034	0.0090	1.8
45	0.5019	0.0050	1.0
Feldspar, 200 mesh and finer			
Fusing temperature, 330° C.; amount of $NaNH_2$, 10 grams			
6[b]	0.4999	0.2550	49.0
8.5	0.4984	0.0212	4.3
11	0.5007	0.0162	3.2
16	0.4996	0.0095	1.9
26	0.5000	0.0027	0.5
46	0.5018	0.0000	0.0
Feldspar, 200 mesh and finer			
Fusing temperature, 210° C.; amount of $NaNH_2$, 20 grams			
30[b]	0.5022	0.2285	45.5
35	0.5035	0.1910	37.9
40	0.5016	0.0512	10.2
50	0.5004	0.0426	8.5
70	0.5061	0.0218	4.3
110	0.5083	0.0137	2.7
Feldspar, 200 mesh and finer			
Fusing temperature, 240° C.; amount of $NaNH_2$, 20 grams			
21[b]	0.5006	0.2566	51.0
23.5	0.5026	0.1986	39.5
31	0.5003	0.0665	13.3
41	0.5022	0.0326	6.5
61	0.5000	0.0170	3.4
101	0.5030	0.0090	1.8
Feldspar, 200 mesh and finer			
Fusing temperature, 270° C.; amount of $NaNH_2$, 20 grams			
16[b]	0.5028	0.2296	45.7
18.5	0.5003	0.1714	34.3
21	0.5018	0.0857	17.1
26	0.5020	0.0434	8.6
36	0.5011	0.0292	5.8
46	0.5008	0.0125	2.5
56	0.5024	0.0059	1.2
Feldspar, 200 mesh and finer			
Fusing temperature, 300° C.; amount of $NaNH_2$, 20 grams			
12[b]	0.5032	0.2623	52.3
14.5	0.5000	0.0427	8.5
22	0.5034	0.0166	3.3
32	0.5004	0.0049	1.0
42	0.5040	0.0027	0.3
Feldspar, 200 mesh and finer			
Fusing temperature, 330° C.; amount of $NaNH_2$, 20 grams			
8[b]	0.5010	0.2762	55.1
10.5	0.4977	0.0106	2.1
13	0.4955	0.0045	0.9
18	0.5040	0.0023	0.45
28	0.4990	0.0003	0.06
Feldspar, 200 mesh and finer			
Fusing temperature, 360° C.; amount of $NaNH_2$, 20 grams			
7[b]	0.5010	0.2744	55.1
9.5	0.5000	0.0080	1.6
17	0.5025	0.0033	0.6
27	0.5010	0.0005	0.1
Feldspar, 115 to 150 mesh			
Fusing temperature, 330° C.; amount of $NaNH_2$, 18 grams			
8[b]	0.4495	0.2320	51.6
13	0.4334	0.0418	9.6
28	0.4422	0.0153	3.5
68	0.4939	0.0074	1.5
188	0.4558	0.0028	0.6
Feldspar, 150 to 170 mesh			
Fusing temperature, 330° C.; amount of $NaNH_2$, 16 grams			
9	0.3864	0.0899	23.1
17	0.3835	0.0287	7.4
67	0.3767	0.0040	1.1
Feldspar, 150 to 170 mesh			
Fusing temperature, 330° C.; amount of $NaNH_2$, 16 grams; amount of NaOH, 0.4 gram (2.5%)			
9	0.3864	0.0886	22.9
17	0.3823	0.0273	7.1
67	0.3823	0.0030	0.8
Glass-sand, 200 mesh and finer			
Fusing temperature, 330° C.; amount of $NaNH_2$, 20 grams			
8[b]	0.5005	0.0020	0.4
10.5	0.5048	0.0018	0.36
13	0.5000	0.0013	0.26
18	0.5050	0.0009	0.18
28	0.4993	0.0000	0.00
Alundum, 150 to 200 mesh			
Fusing temperature, 360° C.; amount of $NaNH_2$, 20 grams			
13	0.5085	0.5020	98.7
577	0.4980	0.4167	84.1
Alundum, 200 mesh and finer			
Fusing temperature, 330° C.; amount of $NaNH_2$, 20 grams			
12	0.4995	0.4483	89.8
427	0.5001	0.1776	35.4

[a] Reckoned from time at which the crucibles were introduced into previously heated muffle.
[b] Sodium amide has just melted at this point.

It is possible to avoid the use of a muffle, provided the inner crucible be fitted with a nickel cover carrying a nickel tube through which a slow stream of ammonia passes during the fusion.

The cooled inner nickel crucible and its contents (and also the outer crucible, if sodium amide has crept into it) are placed in a 500-cc. casserole, which is partly filled with 95 per cent alcohol and then covered with a watch glass. Small quantities of water are added from time to time as the reaction subsides. The subsequent analysis of the dissolved fusion is carried out according to the usual methods (*6*).

The muffle furnace, to which reference has been made, consists of a rectangular monel metal box (15 × 8 × 6 inches, inside dimensions) closed by a hinged door. To the outside of this box are spot-welded eight 14-inch chromolox heating units, the whole being well insulated against heat losses with asbestos. The top of the furnace carries three holes which are used, respectively, for a thermometer well and for the introduction and removal of ammonia. It is permissible to use an ordinary gas-fired muffle, but it is recommended that it be lined with a monel metal or nickel box, through which a current of ammonia can be passed.

Conclusions

The foregoing work definitely shows that fused sodium amide may be used to open up silicates, glasses, and certain refractories as a preliminary step in their quantitative analysis. The temperature and time of fusion, the size of the particles of the substance to be analyzed, and other factors play a very important part in the course of the reactions. The experimental findings may be summarized as follows:

Silicon can be determined accurately in commercial silicon, ferro-silicon, feldspar, bauxite, soda and Pyrex glasses, burnt refractory, and at least in one variety of clay, after fusion for varying periods of time with sodium amide at a temperature of 330° C. (Higher temperatures may cause undue volatilization of sodium amide.) The specimens for analysis must be finely ground, preferably to 200 mesh per inch or finer (Table II). In the case of an easily fusible silicate, feldspar, the minimum fusion time, at the end of which sensibly complete decomposition of the 200-mesh material has taken place, is about 30 minutes. It is recommended that the time of fusion of material of unknown behavior be 2 to 3 hours at 330° C. Alundum (Table II) is not completely broken down by fused sodium amide under the optimum conditions in 9 hours, and it therefore cannot be analyzed by the methods described without an undue expenditure of time. The fact that a substance containing alumina is slowly attacked by fused sodium amide is of some interest, since pure alumina has been reported by Fernelius (*4*) to remain unattacked at 375° C. The alumina used in the latter experiments was not ground.

Zirconia of 200 mesh is slowly and completely attacked by fusing with sodium amide for 4 hours at 330° C.

It is rarely necessary to eliminate traces of nickel from the aqueous solutions of the sodium amide fusions, since a number of blank determinations showed this to be present in amounts of 0.3 mg. or less per analysis (dimethylglyoxime test).

Table III. Comparison of Analysis of Silicon and Ferrosilicon Fused with Sodium Amide and with Sodium Carbonate

Substance[a]	Fusion Time at 330° C.	Weight of Sample	Sodium Amide Fusion Weight of SiO_2	Sodium Amide Fusion Per cent of Si	Sodium Carbonate Fusion Per cent of Si
	Hours	*Gram*	*Grams*		
Ferrosilicon	9	0.4980	0.8027	75.4	75.6
		0.4944	0.7996	75.6	
Ferrosilicon	4	0.5033	0.7709	71.9	75.6
		0.4998	0.7667	71.7	
Ferrosilicon	5	0.2001	0.3083	72.0	75.6
Silicon	9[b]	0.4887	1.0353	96.9	96.7
		0.4968	1.0268	96.73	
Silicon	4	0.4871	0.9258	87.06	96.8
		0.4980	0.9252	86.8	

[a] 200 mesh. 20 grams of $NaNH_2$ used per analysis.
[b] 5 per cent NaN_3 added.

In all the fusions which have been considered in this article, it is probable that mixed aquo-ammono silicates, aluminates, etc., are primary products of the reactions, but whether these are further converted to sodium ammono silicates, aluminates, etc., is a matter of conjecture.

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Inclusion of Rarer Metals in Elementary Qualitative Analysis

I. Inclusion of Tungsten and Molybdenum in Groups I and II

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During more than a hundred years (*3*) the list of metals found in the general scheme of elementary qualitative analysis has remained practically unchanged. In the light of the growing commercial importance of some metals not found in the original list, it has seemed advisable to introduce a few of the more important rarer metals by modifying and simplifying certain procedures from schemes for the analysis of the rare elements (*1, 2, 4*) and incorporating them into the scheme for the commoner ones. The detection of tungsten in group I and of molybdenum in group II is described in this paper, and detection of titanium and vanadium in group III will be described later.

Stock solutions of the common ions are made up in the customary manner. For tungsten and molybdenum, the alkali salts of the tungstate and molybdate are dissolved in water and diluted to the proper concentration.

Detection of Tungsten in Group I

The sample, which may include a suspended precipitate, is treated with dilute hydrochloric acid until precipitation appears complete, and 5 cc. of the acid are added in excess. This mixture is warmed just below the boiling point for 2 or 3 minutes, and cooled, in order to make the precipitate of tungstic acid or tungstic oxide more complete. If the material is boiled, some or all of the mercurous ions will be oxidized, provided nitrates are also present. The cooled mixture is filtered two or three times through the same paper if necessary to obtain a clear filtrate which is reserved for later groups. Certain acid ions—namely, arsenate, arsenite, phosphate, borate, oxalate, tartrate, vanadate, and to a less extent acetate—interfere with the completeness of the tungsten precipitation, so that combinations of these with tungsten should be avoided. The separation of the lead chloride by hot water and the identification of mercurous mercury by the use of ammonium hydroxide are accomplished in the customary manner. The ammoniacal filtrate from the mercury will contain the silver and the tungsten. This solution is then made nearly neutral with dilute hydrochloric acid, and enough ammonium hydroxide is added just to redissolve any precipitate that may have appeared. The silver may now be identified and separated by the addition of a soluble iodide followed by filtration. In the presence of a large excess of ammonia, the precipitated silver iodide is colloidal, and it is difficult to remove it by filtration. This test for silver has been shown to be fully as sensitive as the usual one using nitric acid to precipitate the silver chloride. After filtration, the solution is evaporated to a small volume, acidified with dilute hydrochloric acid, and treated with 3 cc. of stannous chloride. After the mixture has been heated to boiling, 3 cc. of concentrated hydrochloric acid are added, and the mixture is again boiled. The formation of tungsten blue proves the presence of tungsten.

Test solutions were run by this method using widely varying concentrations of the constituent ions. Tungsten was found correctly in all cases where there was as much as 10 mg. of this metal in the solution, in the presence of even as much as 400 mg. of other metals of group I. In the hands of a class, satisfactory results were obtained with samples in which the concentration of each constituent present was approximately tenth normal.

Detection of Molybdenum in Group II

Molybdenum belongs in the arsenic division of the hydrogen sulfide group. In order to effect a satisfactory separation of the molybdenum sulfide, however, the procedure for the precipitation of the group should be modified.

The filtrate from group I is neutralized with ammonium hydroxide and is made slightly acid with dilute hydrochloric acid. To this are added 2.5 cc. of concentrated hydrochloric acid, 1 gram of ammonium iodide, and enough water to make a total volume of 100 cc. This mixture is then saturated with hydrogen sulfide in the cold in a pressure precipitation flask and the flask, loosely stoppered, is placed in a beaker of boiling water. When the water has again reached boiling temperature, boiling is continued for 4 or 5 minutes, after which the mixture is cooled, resaturated with hydrogen sulfide, and filtered.

This procedure has been shown to precipitate satisfactorily all the members of this group. Of the commonly mentioned ions that interfere with the precipitation of molybdenum sulfide, the presence of phosphate must be avoided, because of the formation of a complex compound that prevents

precipitation of the sulfide. In the presence of arsenic in the trivalent or the pentavalent state, interference is experienced only when there is a small amount of molybdenum with a relatively large amount of arsenic. The precipitation is satisfactory if there is not much more than two or three times as much arsenic as molybdenum. Reducing ions, such as stannous tin, should be avoided on account of their action upon the molybdate, which reduces the sensitivity of the sulfide test. Tests were run which showed that the addition of the iodide is necessary for the precipitation of arsenic, and that it does not interfere with precipitation of molybdenum.

In the usual treatment of the residual sulfides of group II with ammonium polysulfide, molybdenum dissolves as $(NH_4)_2MoS_4$, and from this the sulfide may be reprecipitated by the use of dilute hydrochloric acid, along with the other sulfides of this division. When the antimony and stannic sulfides have been dissolved out in warm concentrated hydrochloric acid, the remaining sulfides of arsenic and of molybdenum are dissolved in warm dilute nitric acid. This solution is then made ammoniacal and the arsenic is precipitated by the addition of magnesia mixture. The solution must be stirred vigorously to be sure that the arsenic does not remain in a supersaturated solution. After the removal of the arsenic by filtration, the molybdenum will be present in the solution as ammonium molybdate. If this is now acidified with dilute hydrochloric acid and treated with ammonium or potassium thiocyanate in the cold, followed by a few drops of stannous chloride, a deep red solution of $MoO(CNS)_6$ is formed, proving the presence of molybdenum. Any iron that may be present as an impurity will be reduced by the stannous chloride and will not interfere with the test.

Test solutions with varying quantities of other constituents were analyzed successfully for molybdenum. A positive test for molybdenum was obtained from a solution of 20 mg. of molybdenum (as metal) in the presence of a total of 600 mg. of other metals such as antimony, mercury, copper, and cadmium. A weaker test was obtained in the analysis of a similar solution including also 100 mg. of arsenic in the form of sodium arsenate. For student use, however, the proportion of molybdenum to other constituents should be more comparable. (Under these latter conditions satisfactory results have been obtained with a class of second-year chemistry students.)

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New Absorption Tube

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A NEW type of absorption tube, which has been designed for the determination of hydrogen in ultimate analysis by combustion, consists of three glass tubes, joined together to form a single unit, and so arranged as to facilitate the cleaning and filling of the apparatus.

In preparing the apparatus for use, the ground-glass stoppers *E* are removed and the tubes filled to the leveling mark *D* with concentrated sulfuric acid by means of a finely drawn out pipet or buret, care being taken to remove any sulfuric acid which may adhere to the ground surface before lubricating. It has been found advisable to use a stiff lubricant for the stoppers, as a sudden evolution of gas may raise the stoppers when a lighter lubricant such as vaseline is used. Sulfuric acid is used because of its great affinity for water, and in order that the rate of the flow of gas may be observed.

The smaller tube is filled with cotton wool, coarsely powdered anhydrous copper sulfate, and granular magnesium perchlorate trihydrate. The anhydrous copper sulfate acts not only as an absorbent but as an indicator to warn of the exhaustion of the reagents by turning a blue color.

The inlet tube is loosely packed with glass wool, to act as an additional trap to any sulfuric acid which might be carried over during the operation.

When ready for use the apparatus weighs approximately 100 grams and can be used on any chemical balance. The apparatus is weighed and the inlet tube *F* is joined flush with the outlet tube of the furnace by means of rubber tubing. At the end of the operation the caps are replaced and the apparatus is again weighed, the increase in weight by the following equation giving the percentage of hydrogen in the sample:

$$\frac{11.19 \times \text{increase in weight}}{\text{weight of sample}}$$

Ten samples of coal were determined in duplicate, in each case checking within 0.0015 gram, without changing the absorbent. The advantage of this tube over a train of calcium chloride tubes as commonly used is at once apparent. It is strong and rugged, although lightly made; it is self-contained; and a single weighing takes the place of a number of weighings, which results not only in greater accuracy but in a considerable saving of time.

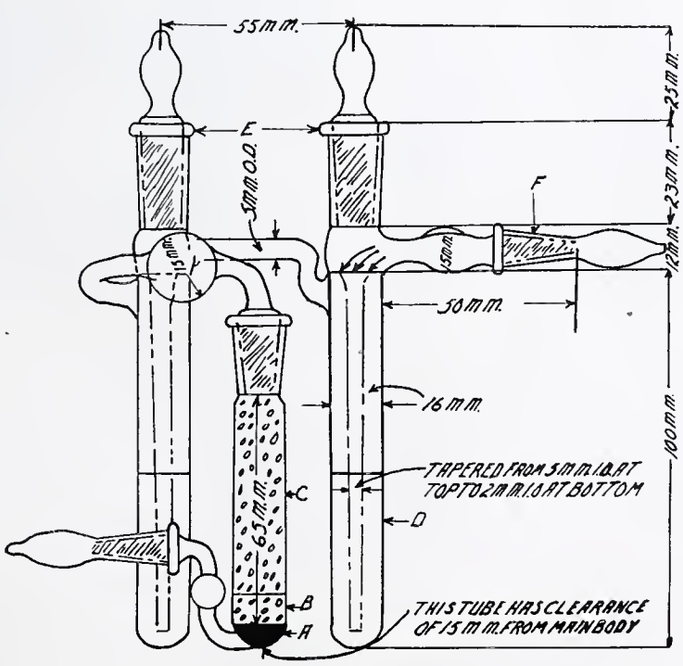

Figure 1. Diagram of Apparatus

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Determination of the Acids of Plant Tissue

II. Total Organic Acids of Tobacco Leaf

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The organic acids of plant tissues can be quantitatively extracted by ether, provided the material is acidified to approximately pH 1 with sulfuric acid. The extract so obtained contains no significant amounts of organic bases or of mineral acids, with the exception of nitric acid. The quantity of organic acids can be determined in the presence of the nitric acid by titration between the limits pH 7.8 and 2.6, according to the principle of the method of Van Slyke and Palmer, by means of a quinhydrone electrode and potentiometer system. Under the conditions adopted oxalic acid behaves as a monobasic acid, a method is therefore provided whereby the oxalic acid can be independently determined and the necessary correction calculated. The other acids usually encountered are titrated to the extent of approximately 90 per cent. A correction factor applicable to the acids that occur in largest amount in tobacco leaf tissue is given. Only a minor modification of this factor would be required to permit the application of this method to other tissues.

Aqueous extracts of plant tissues have long been known to contain considerable proportions of organic acids. Citric, malic, tartaric, succinic, and oxalic acids are usually the most abundant, and the wide distribution of these particular acids is well recognized. Surprisingly little that is definite is known of the functions of these organic acids in the plant; their chemical relationships to each other and to the protein and carbohydrate metabolism are still largely matters of speculation.

The determination of the organic acids of plant tissues presents an analytical problem of considerable complexity because of the wide variety of acidic substances that may be present. Furthermore the organic acids must, in general, be estimated in the presence of more or less mineral acid, a circumstance that places restrictions on the use of ordinary titration methods. The present communication describes a method whereby the total acidity due to these organic acids may be estimated. This method, used in conjunction with methods for the determination of the individual acids, yields data of considerable value for the interpretation of results obtained in studies of organic acid metabolism. The method is founded on the observation that the organic acids, together with the nitric acid contained in tobacco leaf tissue, can be extracted by ether in an efficient extraction apparatus, provided the tissue is previously acidified with sulfuric acid. The acidity due to the organic acids can then be determined by titration between the pH limits 7.8 and 2.6, according to the principle of the method of Van Slyke and Palmer (*5*) for the determination of the organic acids of urine. Owing to the dark color of the solutions usually obtained from plants, this titration is best conducted with the aid of a quinhydrone electrode.

Preparation of Organic Acid Extract

In order to ascertain the amount of 4 *N* sulfuric acid required to acidify the tissue to pH 0.6 to 0.9, preliminary trials are carried out in which a small quantity (1 cc.) of the acid is mixed with 0.5 gram of the tissue and sufficient water is then added so that a thin suspension of the powdered material can be transferred to the quinhydrone electrode vessel for measurement; suitable changes in the quantity of acid are made as suggested by the result of the first test, and the amount required for 2.0 grams of the tissue is calculated.

A 2.00-gram sample of the dry and finely ground tissue is then intimately mixed with this amount of 4 *N* sulfuric acid, 3.5 grams of asbestos are added and thoroughly incorporated, and the mixture is transferred, with the aid of conical funnel constructed of paper and impregnated with paraffin, to a 26 × 60 mm. Schleicher and Schüll extraction thimble. Small particles of material remaining are brushed in, and the glassware and funnel are wiped with a small piece of moistened surgical cotton which is then used as a plug for the thimble. The thimble is placed in a siphon tube of the type designed for rubber analysis (Eimer and Amend catalog No. 30754), a short thin glass rod is thrust between the paper and the glass tube to provide a space for the accumulation of ether, and the tube is suspended by a loop of fine galvanized iron wire close under the spiral coil of the metal condenser. The condenser is furnished with a soft cardboard gasket and is placed on the conical extraction flask, being held firmly in position by three spring paper clips. The flask contains about 150 cc. of specially prepared ether. Extraction is carried out on an electric hot plate, so adjusted that the ether siphons back at least 40 times an hour, for 17 to 20 hours.

The ether for this extraction is prepared by being washed three times with water to remove alcohol; each liter of ether is subsequently shaken vigorously with 200 cc. of 10 per cent sodium hydroxide and 5 to 10 grams of powdered potassium permanganate (excess), and is then distilled. This treatment is essential for satisfactory results, and it is important that the ether should have been prepared not more than 24 hours before use.

The ether extract is treated with 25 cc. of carbon dioxide–free water (previously boiled and stored in a bottle protected by soda lime), and 2 cc. of carbon dioxide–free, approximately 5 *N* sodium hydroxide. The flask is gently agitated to insure removal of the acids into the aqueous phase, and the ether is carefully distilled off. The aqueous solution is transferred to a 100-cc. flask and diluted to the mark with carbon dioxide–free water.

This solution is "the organic acid fraction." Parallel with the determination an equal quantity of ether is refluxed for the same period of time, and subsequently carried through the same series of operations; the solution obtained is referred to below as the "ether blank."

Electrometric Titration of Organic Acids

The potentiometer circuit used in this laboratory employs a Leeds and Northrup student's hydrogen-ion potentiometer. A galvanometer shunt of approximately 8700 ohms resistance is provided; this is indispensable for rapid titration. The reference elctrode is a saturated calomel half-cell; connection between this and the titration vessel is established by an agar bridge prepared according to Michaelis and Fujita (*3*).

The electrodes are constructed by sealing 1 cm. of No. 22 platinum wire into the end of a 10-cm. length of 4-mm. diameter soft glass tubing. These electrodes must be free from cracks. They are cleaned by being boiled a short

time in 50 per cent nitric acid, and then in 5 to 10 per cent sodium acid sulfite (*1*), and are stored under distilled water. Before use, each electrode is allowed to stand at least 5 minutes in water that contains a little quinhydrone. Each electrode should be checked against a known buffer solution, or by titration of a standard solution of an organic acid; any that show a sluggish end point should be discarded, the fault in such cases being usually a minute crack.

To conduct the titration, a 10-cc. aliquot of the "organic acid fraction" is transferred to a 50-cc. beaker that has a calibration mark at 25 cc., and 2 drops of a 1 per cent alcoholic solution of phenolphthalein are added; 0.5 *N* acid is added from a pipet until the red color is discharged; an electrode is introduced and 10 drops of quinhydrone solution are added.[1] The positive wire from the potentiometer is connected to the platinum electrode, the negative wire to the saturated calomel half-cell, and the electrical circuit is completed by means of an agar bridge. The potentiometer circuit is then checked for balance, and the potentiometer scale is set at 0.00 millivolt (pH 7.8). Dilute alkali (0.05 *N*) is added drop by drop until no deflection of the galvanometer is obtained after careful stirring of the contents of the beaker. The solution is now at pH 7.8. The potentiometer is adjusted to 301 millivolts (pH 2.6), and 0.1 *N* nitric acid is rapidly added from a buret with stirring until the galvanometer deflections become small, and then drop by drop to zero deflection. The solution is finally diluted to the 25-cc. mark with carbon dioxide–free water, and the titration is carefully completed. The 0.1 *N* nitric acid used represents the titration value of the organic acids, and of 25 cc. of water, between the limits pH 7.8 to 2.6. A 10-cc. aliquot of the "ether blank" solution is then titrated with the same electrode, and the titration value obtained is subtracted from that of the organic acid fraction.

Oxalic Acid Correction

Oxalic acid behaves as a monobasic acid under the conditions described, only the weaker acid group entering into reaction; consequently it is necessary to carry out an independent determination of oxalic acid in order to correct the final result for the whole of the acidity due to this acid.

To this end a 25-cc. aliquot of the organic acid fraction is acidified to Congo red with 0.5 *N* hydrochloric acid, the precipitate that forms is allowed to flocculate and is filtered off on asbestos in a Gooch crucible and washed with water. A drop of methyl red solution is added to the clear filtrate. Ammonium hydroxide is added to a faint alkaline reaction, 2 to 3 cc. of glacial acetic acid are added, followed by 5 cc. of 10 per cent calcium chloride solution. After being allowed to stand at least 2 hours the calcium oxalate is filtered on asbestos in a Gooch crucible, and is washed with a little very dilute ammonium hydroxide. Crucible and contents are then transferred to a 100-cc. beaker, 5 cc. of 50 per cent sulfuric acid and 20 cc. of water are added, and the solution is heated to boiling and titrated with 0.02 *N* potassium permanganate. The oxalic acid is calculated from the relation, 1 cc. of 0.02 *N* permanganate is equivalent to 0.9 mg. of anhydrous oxalic acid.

Under these conditions oxalic acid can be rapidly and accurately estimated in the presence of a large excess of citric acid. Data in support of this statement have been given by Vickery and Pucher (*6*).

Calculation of Titration Data

The proportion of an organic acid that is titrated between two given hydrogen-ion activities can be calculated from the dissociation constants of the acid. Calculations with respect to the acids that require consideration in the titration of leaf extracts, and to the pH limits the authors have arbitrarily adopted, are shown in Table I. The titration value of a leaf extract obtained as described above, expressed in terms of 0.1 *N* acid, contains an error owing to the fact that none of the common leaf acids titrate to the extent of 100 per cent. A further correction for oxalic acid must also be applied.

[1] Acetone is treated with aqueous sodium hydroxide and excess of potassium permanganate and distilled; 0.167 gram of quinhydrone is dissolved in 3 cc. of this acetone and stored in a test tube fitted with a medicine dropper. The solution should be discarded if it has stood more than 3 days.

It is convenient to express the acidity in terms of milliequivalents per 100 grams of dry tissue; substitution of the analytical values into the following equation yields the desired result:

$$\left[(A - B)\,50 - \frac{C}{0.09}\right] 1.09 + \frac{2C}{0.09} = M.E.$$

A = cc. of 0.1 *N* nitric acid required in the titration of a 10-cc. aliquot of the "organic acid fraction"
B = cc. of 0.1 *N* nitric acid required for a 10-cc. aliquot of the "ether blank"
C = per cent of oxalic acid in the dry tissue
$M.E.$ = milliequivalents of organic acid in 100 grams of dry tissue

$A - B$ gives the titration value of the acids in one-tenth of a 2-gram sample of tissue in terms of 0.1 *N* acid; the factor 50 converts this to milliequivalents per 100 grams; division of C by 0.09 converts the percentage of oxalic acid ($M.W. = 90$) to milliequivalents per 100 grams, if oxalic acid is considered as a monobasic acid. The factor 1.09 is calculated from the observations (Table I) on the titration of malic and citric acids and represents as close an approximation as is necessary to the ratio between the actual titration value over the selected pH range, and the true amount of organic acidity present in tobacco leaf tissue. In the case of tissues that contain tartaric acid as an important constituent a somewhat larger factor would be required. The first term of the equation, then, represents the acidity due to the organic acids exclusive of oxalic acid; to this is added the acidity of oxalic acid calculated as a dibasic acid.

Experimental Foundation of Method

The selection of the quinhydrone electrode rather than the hydrogen electrode scarcely needs justification in view of the convenience and wide applicability of this system. The choice of the upper limit of the titration (pH 7.8) was made because, at reactions more alkaline than this, the quinhydrone electrode changes polarity and becomes increasingly unreliable. The lower limit was arbitrarily selected because sharp end points could be obtained and the blank correction was not unduly large. Titration to pH 2.3 was less satisfactory.

Table I. Proportions of Certain Acids Titrated between Limits pH 7.8 and 2.6

Acid	Dissociation Exponents	Acid-Free at pH 7.8	Acid-Free at pH 2.6	Proportion Found by Titration
	pK	%	%	
l-Malic	3.48 5.11	0.009	93.8	93.5
Citric	3.08 4.39 5.49	0.005	89.7	90.0
Oxalic	1.42 4.39	0.00	49.6	50.5
d-Tartaric	3.00 4.39	0.08	85.0	84.0
Fumaric	3.03 4.49	0.00	83.9	83.5
Maleic	1.93 6.58	0.00	58.8	56.0
Succinic	4.18 5.57	0.05	98.6	98.5
Lactic	3.85	0.00	94.8	..
Acetic	4.73	0.008	99.3	..
Malonic	2.80 5.68	0.00	76.0	..
Boric	9.2	96.4	100.0	5.0
Phenol	10.0	99.3	100.0	0.2
$H_3PO_4[H(NaHPO_4)]$	2×10^{-7}	7.3	100.0	90.0

The final adjustment of the end point must be made in the presence of a constant volume of water. Experiments in which different amounts of water were titrated showed that a variation of ±1 cc. of water involved a variation of ±0.03 cc. of 0.1 *N* acid; consequently, if a precision of the order of 0.1 cc. of acid is sought, the final volume must be adjusted to within 3 cc. of the standard volume selected. This is easily accomplished by calibrating a 50-cc. beaker at 25 cc., and making the final adjustment of the volume with a little

care. The final increment of acid required, if the titration is conducted as described, is usually less than 0.5 cc.

Nitric acid was selected as the titrating reagent because it is slightly stronger than hydrochloric acid.

Table I gives the results of titrations of a number of acids, most of which may be encountered in work with plant extracts; of these the first four are commonly the most plentiful. The titrations were conducted on 0.1 *N* solutions of the acids. Oxalic and maleic acids titrate as monobasic acids; only the former need be considered here, however, as maleic acid has not hitherto been detected in plants. In tobacco leaves malic, citric, and oxalic acids predominate, these three usually making up at least 70 per cent of the total organic acid acidity. The present discussion of the correction factor to be employed will be restricted to results secured with this tissue. The application of the method to extracts from another tissue of different organic acid make-up would require, however, only a slightly modified factor.

The ether extract obtained as described from tobacco leaf contains no bases that can be precipitated by silicotungstic acid. The chief mineral acid present is nitric acid which is quantitatively extracted from the tissue under these conditions (*4*). Traces of other nitrogenous substances are also present, but these, on the average, amount to only 3.6 mg. of nitrogen in the extract from 2 grams of dry tissue, and their influence on the titration can be neglected. Carbonic, sulfuric, phosphoric, and hydrochloric acids, if present, would affect the titration. Carbonic acid is expelled during the extraction period, and its subsequent advent is carefully guarded against. A trace (0.4 to 0.6 mg.) of sulfuric acid is, in fact, extracted, but control experiments indicated that the titration of this between the limits adopted would consume only about 0.01 cc. of 0.1 *N* acid. Ordinarily hydrochloric acid is present in plant tissues in very small amounts and, since this acid is titrated only to the extent of 3 to 5 per cent, no significant error can enter. Many experiments designed to test the effect of phosphoric acid on the titration showed that the presence of this acid can also, in general, be neglected. Phosphoric acid is extracted to the extent of about 15 per cent under the conditions described. A 2-gram sample of tobacco leaf tissue usually yielded from 3 to 6 mg. of phosphoric acid in the extract, and the titration of this quantity of phosphoric acid under standard conditions required from 0.5 to 1.0 cc. of 0.1 *N* acid. Thus the error in the titration of a 10-cc. aliquot of the organic acid fraction might be from 0.05 to 0.1 cc., or from 2.5 to 5 per cent too high, if the titration value is 2 cc. Ordinarily the titration value is somewhat more than this, so the phosphoric acid error is not great. Should occasion arise, however, it can be easily eliminated by the introduction of a correction. To this end an aliquot part (10 to 25 cc.) of the fraction is acidified with sulfuric acid, filtered, neutralized, and the phosphoric acid in it is determined by the method of Fiske and Subbarow (*2*). The correction is calculated from the relation

$$\frac{\text{mg. P} \times 3.16}{5.9} = \text{cc. 0.1 } N \text{ acid required in aliquot used}$$

and is subtracted from the titration value observed.

In order to test the completeness with which citric, malic, and tartaric acids can be extracted by ether from aqueous solution and subsequently recovered by titration, a mixture of approximately equal parts of these three acids was prepared of such concentration that a 5-cc. aliquot part of the solution should contain the equivalent of 25.03 cc. of 0.1 *N* acid. Seven titrations gave an average titration value of 21.98 cc. with a maximum variation of ±0.2 cc. Similar quantities of the solution were acidified to pH 0.8, and were mixed with asbestos in the usual way, dried in a vacuum desiccator until the material could be conveniently transferred to the extraction thimble, and were then extracted with ether for various times. The results are shown in Table II.

Table II. Extraction and Titration of a Mixture of Malic, Citric, and Tartaric Acids

(If these acids titrated to the extent of 100 per cent the titration value would be 25.03 cc. Data are expressed in cc. of 0.1 *N* acid and are corrected for water blanks.)

Time of Extraction	Titration Value between pH 7.8–2.6	Recovery
Hrs.	*Cc.*	%
0	21.98	87.9
4	20.88	83.4
6	20.75	83.2
8	21.75	86.9
12	22.48	89.7
16	22.08	88.7
24	22.13	88.4
72	22.25	88.9
93	22.20	88.7
120	22.25	88.9

It is clear that most of the acid is extracted in a relatively short time and that constant titration values are obtained after 12 hours of extraction. A 16- to 20-hour period has therefore been adopted for practical work. The average recovery of the acids after 16 hours' extraction was 88.7 per cent. Calculation from the data for the dissociation constants of these acids shown in Table I indicated that a 90.8 per cent recovery might have been expected; evidently therefore these acids can be satisfactorily extracted and estimated by the technic described.

As a further test of the method a standard solution of citric acid, acidified with sulfuric acid to pH 1, was treated as described, and extracted for 16 hours. The results are recorded in Table III. The average recovery was 97.7 mg. from 96 mg. taken. Analysis of the extracts by the pentabromoacetone method indicated the presence of 94 to 97 mg. in the different samples. The method may therefore be expected to yield results of an accuracy of ±3 per cent.

Table III. Extraction of Citric Acid

Citric Acid Taken	Titration Value	Citric Acid Found[a]	Citric Acid Found, Corrected[b]
Mg.	*Cc.*	*Mg.*	*Mg.*
96	14.2	90.9	100.0
96	13.8	88.3	97.1
96	13.7	87.7	96.5
96	13.8	88.3	97.5

[a] Cc. 0.1 *N* acid × 6.4 = mg. citric acid.
[b] Corrected on the assumption that 90 per cent of the citric acid is titrated between pH 7.8 and 2.6.

Titration of Acids of Tobacco Leaf

In order to establish the conditions for quantitative extraction of organic acids from leaf tissue, 2-gram samples of cured tobacco leaf, and of fat-free tobacco-seed meal, were extracted before and after the addition of citric, or of oxalic acid. Although only a small quantity of acid was added to the leaf tissue, the recoveries, shown in Table IV, were satisfactory.

Table IV. Recovery of Organic Acids Added to Plant Tissue

(Data are expressed in cc. of 0.1 *N* acid)

Sample	Organic Acids: Originally present	Added	Found	Recovered		Recovery Theory
	Cc.	*Cc.*	*Cc.*	*Cc.*	%	%
Cured tobacco	11.1	1.25[a]	12.15	1.05	84	90
Cured tobacco	11.1	1.25	12.20	1.10	88	
					Av. 86	
Cured tobacco	9.9	2.50[b]	11.2	1.3	52	50
Cured tobacco	9.9	2.50	11.1	1.2	48	
Cured tobacco	9.9	2.50	11.3	1.4	56	
Cured tobacco	9.9	2.50	11.1	1.2	48	
					Av. 50.8	
Tobacco-seed meal	1.2	6.25[a]	7.0	5.8	93	90
Tobacco-seed meal	1.2	12.50	12.6	11.4	91	
Tobacco-seed meal	1.2	12.50	12.6	11.4	91	
Tobacco-seed meal	1.2	12.50	12.7	11.5	92	
					Av. 91.7	

[a] Citric acid added.
[b] Oxalic acid added.

Table V. Organic Acid Content of Cured Tobacco Leaf

Sample	Titration Value	Titration Value, Ether Blank	Organic Acids
	Cc.	*Cc.*	*M. E./100 Grams*
627	4.50	0.70	190
	4.55	0.75	190
628	5.45	0.75	235
	5.50	0.75	237.5
623	4.60	0.75	192.5
	4.45		185.0
624	4.80	0.75	202.5
	4.80		202.5
625	4.95	0.70	212.5
	4.95	0.75	210.0
626	3.90	0.75	157.5
	3.90		157.5

Table V shows the results of a series of duplicate determinations on a number of samples of cured tobacco. These data are presented to illustrate the very satisfactory reproducibility of the results of the titration.

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Pectin Studies

II. Sugar-Acid-Pectin Relationships and Their Bearings upon Routine Evaluation of Apple Pectin

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The interrelationship of acid concentration, sugar concentration, and pectin concentration in apple pectin jellies is outlined, and it is shown that the optimum pH of apple pectin jellies prepared by the usual method varies with the concentrations of acid and of pectin. The changes in the position of the optimum pH with variation in pectin concentration change the slope of the logarithmic jelly-strength–pectin-concentration curves to such an extent as to render exact evaluation difficult.

Apple pectin and citrus pectins of the same commercial grade, or of different grades but used in equivalent amounts in standard jellies, do not result in the same gelometer readings. The elasticity of the apple jellies prevents a sharp break and results in high readings on the instrument and for this reason the standard curves previously given for citrus pectin jellies are not suitable for evaluating apple pectin jellies. An average curve for 100-grade apple pectin indicates a value of 50 Tarr-Baker units for 2.6 grams of pectin in 555 grams of jelly.

A method of preparing apple pectin jellies which apparently obviates most of the difficulties of maintaining optimum acid conditions and which permits ready routine comparisons of samples is described.

In an earlier publication (*3*) Olsen presented a simple routine procedure for the evaluation of citrus pectin, in which the acidity was maintained constant. With apple pectins it is, however, necessary to prepare test jellies at the so-called optimum pH. Where several samples prepared by the same method are to be compared, this is usually accomplished by adding predetermined standard amounts of acid. The acid requirements, however, change with the age of the sample and with the method of preparation, hence when the history of the sample is unknown, it is necessary to determine the optimum acidity. This may involve an extensive series of jellies. A method which would obviate such prior determination should therefore prove of considerable help in the evaluation of samples for routine or research purposes.

The well-known data of Tarr (*6*) and Baker (*1*) suggest such a high degree of sensitivity of apple pectin towards moderate changes in acidity that the routine method proposed for citrus pectins cannot be expected to be applied without modifications in the evaluation of apple pectins. The data of these workers, in so far as they relate to the optimum pH of apple pectin jellies prepared by the usual "hot" method (*5*), are in essential agreement with unpublished data accumulated in the authors' laboratories over a period of years.

The general procedure described by Olsen (*3*) was used in obtaining the data here presented except for such modifications as are mentioned specifically. Two typical jelly-strength curves for alcohol-precipitated apple pectin jellies containing 60 per cent of sugar are shown in Figure 1. Identical series were run with lactic and tartaric acids, using a newly prepared sample of pectin. The two curves coincide closely. Definite pan gelation or curdling occurred in each case at a pH of about 2.55. The authors' observations invariably indicate a progressive change in the optimum pH towards higher acid requirement during storage of samples at ordinary temperatures. Studies were subsequently undertaken to observe the interrelationships of acid, pectin, sugar, and temperature over a range sufficiently wide to permit drawing general conclusions and if possible provide a basis for the simplification of the study and evaluation of samples of apple pectin with varying histories.

Sugar-Acid Relationship

Spencer (*5*) has at some length reviewed the more important data and current hypotheses concerning the roles of sugar and acid in pectin jellies. In 1922 Singh (*4*) showed that with citrus pectin the amount of sugar necessary barely

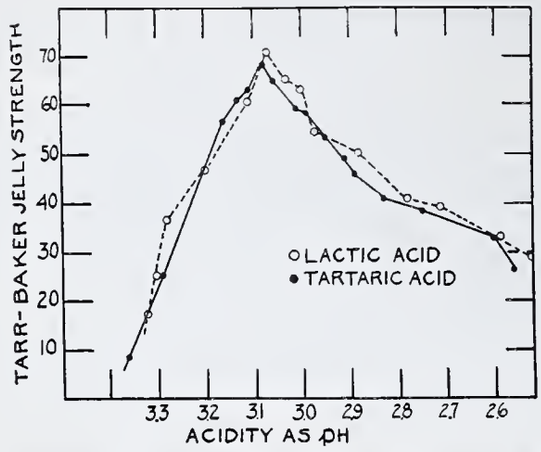

FIGURE 1. EFFECT OF pH ON JELLY STRENGTH OF APPLE PECTIN JELLIES
Usual short-boil method

to form a jelly varied inversely with the acid concentration. Although no attempt was made to determine either pH or optimum acidity for any given sugar concentration, one might reason from Singh's data that the so-called optimum pH would change with variation in sugar concentration. In 1924 Tarr and Baker (*7*), on the basis of data in their Table I, concluded that the greater the hydrogen-ion concentration the more sugar may be added (pp. 10, 19, and 20). Yet on page 8 of the same bulletin they stated that "the sugar concentration could be decreased materially as the hydrogen-ion concentration was increased." It was difficult to reconcile these two statements, the first directly opposite to the view of Singh quoted above, and the second in complete accord with that view. An explanation of the first statement may, however, be derived from a subsequent bulletin by Tarr (*6*), where an optimum pH curve is given for jellies containing 70 per cent of sugar and acidified with sulfuric acid. These jellies appear essentially to duplicate those described in the earlier publication. An optimum pH of about 3.05 is shown.

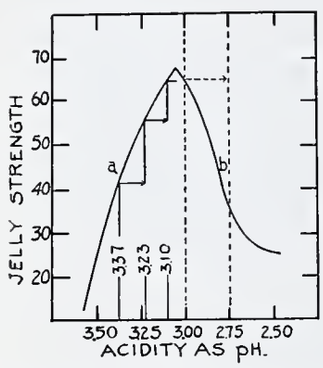

FIGURE 2. EFFECT OF ADDITION OF ACID ON SUGAR-CARRYING CAPACITY OF PECTIN

a, Capacity increased
b, Capacity decreased

The acidities used in Tarr's earlier work were pH 3.37, 3.23, and 3.10. It is at once apparent from a study of this optimum curve why an increase in acid from 3.37 to 3.23 and from 3.23 to 3.10 permitted the pectin to hold more sugar. Each increment of acid brought the pectin nearer to its optimum strength. If, on the other hand, the acidities selected had been on the other side of pH 3.05, say from 3.00 to 2.75, the reverse conclusion would have been reached. Tarr's optimum curve and the manner in which it serves to explain what would otherwise appear as an inconsistency of statement in his earlier publication are shown in Figure 2.

The effect of sugar concentration upon the acid requirement, with pectin concentration maintained constant, was studied in these laboratories within the range of 66 to 56 per cent of sugar. Six series of jellies were prepared, using the general procedure described by Olsen (*3*), except that alcohol-precipitated apple pectin was used instead of citrus pectin.

For each jelly, 50 grams of a concentrated apple pectin solution (Certo) were used. The normal pH of this solution is close to 3.0. Lactic acid was added to obtain the lower pH values and calcium carbonate to obtain the higher values. The effect of the calcium carbonate itself was separately tested and even when added in excessive amounts, followed by proper adjustment of pH, did not appear to be greater than the experimental error of the jelly-strength determinations. The net amount of jelly made in every case was 555 grams and the amount of distilled water varied with varying pectin, acid, and sugar content to give a gross of 585 grams, allowing 30 grams for evaporation in making the jelly. As usual four glasses were poured, and the average of the four determinations on the gelometer recorded as the jelly strength. These are shown in Figure 3.

The pH was determined on the finished jelly following the jelly-strength determinations. The apparatus used for pH determinations on jellies consists of the usual Leeds and Northrup type K potentiometer, type R galvanometer, saturated potassium chloride–calomel half-cell, and gold wire electrode. About 10 grams of jelly are introduced into a small wide-mouth bottle (about 25 cc. capacity) and brought to the same temperature as the calomel half-cell. A small amount of quinhydrone is added, rapidly stirred in with the electrode, and the reading taken at once. The only precautions found necessary are those of adjusting the temperature and adding sufficient quinhydrone to give a permanent brown color.

The readings are corrected for the temperature at which they are taken and the pH is calculated. A very convenient table of correction factors used at the Bureau of Dairy Industry was kindly supplied to the authors through the courtesy of E. O. Whittier.

One of the authors (Beach) has made a comparative study of pH determinations of the pectin-acid solution and of the jellies made therefrom. The determinations made upon the finished jellies were more consistently in accord with the variations observed in jelly strength, although differences were slight.

Curves I, II, III, and V in Figure 3 show clearly the relationship of sugar concentration to optimum acidity in jelly formation. All the curves have the same general shape, rising with increasing acid to an optimum and dropping off upon further addition of acid. The optimum jelly strength is about the same in each case but occurs at a higher pH as the sugar is increased. The 66 per cent curve is imperfect; subsequent observations lead to the belief that one point is in error and that the true curve would follow that indicated by a light dotted line. The curves for series IV and V are less uniform than the others, probably because of the character of the jellies obtained. In series V (56 per cent sugar)

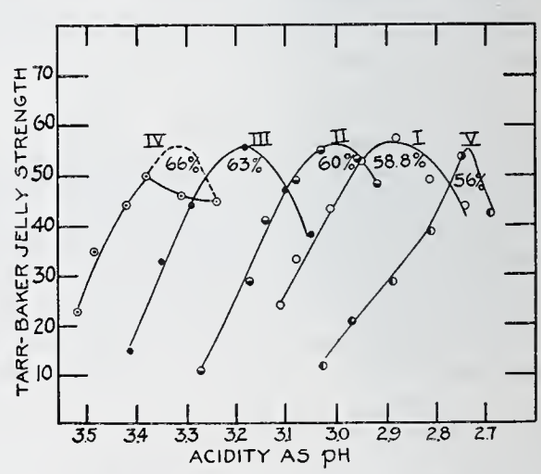

FIGURE 3. EFFECT OF SUGAR CONCENTRATION ON OPTIMUM pH FOR APPLE PECTIN JELLIES

a jelly was obtained which may be described as very tender and crystalline,[1] with a tendency to break apart very easily when removed from the glass. In series IV (high-sugar) the jellies were salvy to the touch and when turned from the glass showed a structure which was not crystalline and did not break apart easily. The plunger of the gelometer did not

[1] By "crystalline" jelly is meant a jelly showing a sharp cleavage and a bright smooth surface where cut or broken apart. Opposite of "salvy."

break through the surface of these high-sugar jellies sharply, but at times sank into the jelly so slowly that it was difficult to obtain exact readings. There was a gradual change in texture throughout the several series from low- to high-sugar concentration, although between series I, II, and III the differences were not pronounced. The curves in Figure 3 suggest the importance of adjusting the pH separately for each selected sugar concentration.

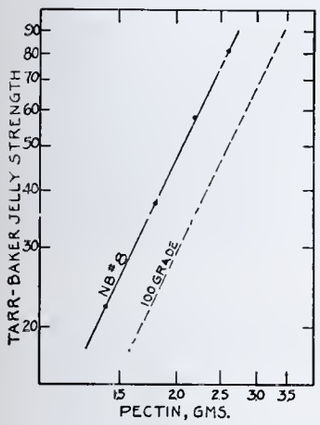

Figure 4. Evaluation of Apple Pectin by Short-Boil Optimum pH Method

Sample N. B. 8 = $100 \times \frac{2.6}{2.05}$ = 127 grade

The results one might obtain by maintaining the acidity constant but varying the sugar concentration are apparent from the same data. Thus, taking the values at which the various curves cross the pH 3.0 line, the results are as follows:

Sugar %	Jelly Strength
56	16
58.8	44
60	56
63	28
66	<20

These figures would indicate an optimum sugar concentration of 60 per cent, but this apparent optimum sugar concentration is simply another manifestation of the changing optimum pH, sugar and acid within limits being compensating factors in the formation of the jelly. It is apparent that one might reach erroneous conclusions from an isolated series like the above.

Evaluation of Apple Pectins

Apple pectins may be evaluated exactly as indicated for citrus pectin except that it is obvious from a study of the above curves that the acidity must be closely adjusted to the optimum. The same logarithmic curve suggested as a standard of comparison for citrus pectin (*3*) has, however, been found unsuitable for evaluating apple pectin. When citrus and apple pectin jellies are compared on the basis of their commercial values (grade based on "finger test"), the gelometer readings for the apple pectin jellies are invariably much higher than the others. This undoubtedly is due to the elastic properties of the apple jelly which permit it to stretch considerably before the plunger is finally forced through.

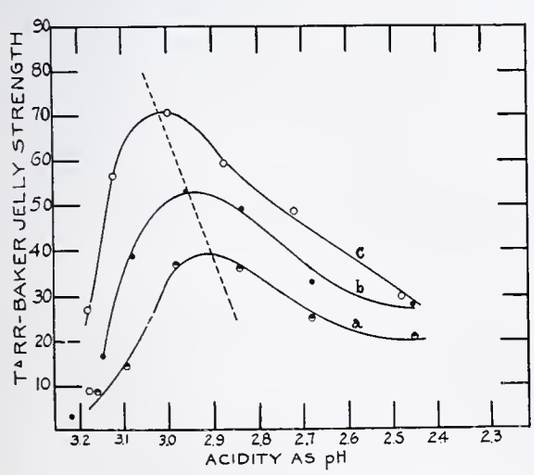

Figure 5. Effect of Pectin Concentration on Optimum pH for Apple Pectin Jellies

a, 2.0; *b*, 2.4; *c*, 2.8 grams of 33 F pectin for 555 grams of jelly. Citric acid used

On the basis of a comparison of a number of commercial samples the authors have found it convenient to define 100-grade apple pectin as a pectin of which 2.6 grams in 555 grams of 60 per cent jelly prepared by the standard method and at the optimum pH will register 50 cm. pressure on the Tarr-Baker gelometer. (Some differences have been observed in readings obtained with different instruments; these were largely caused by slight variations in size of the plunger and of the plunger cap. Each instrument should be checked against a known sample used as standard.)

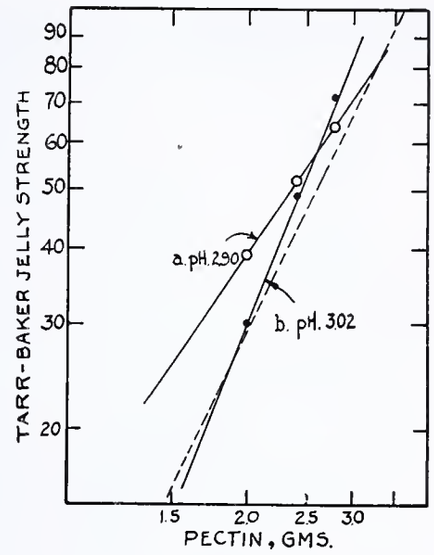

Figure 6. Effect of Shift in Optimum pH with Varying Pectin Concentration on Slope of Logarithmic Jelly-Strength–Pectin-Concentration Curve

Plotted from data in Figure 5

A series of five jellies was made with the standard formula and procedure but using different amounts of apple pectin (sample N. B. 8) with the same amount of acid in each case. This resulted in jellies varying in pH from 2.91 to 3.10. When the weight of the pectin was plotted against gelometer reading on a logarithmic scale the mean of the points gave a straight line. There was, however, not very good correspondence in the points. A second series was therefore made up varying the amount of acid added to give closer agreement in pH values. Table I gives the figures obtained in this series.

Table I. Effect of Pectin Concentration on Jelly Strength

(pH approximately constant)

Pectin per Formula	10 Per Cent Tartaric Acid	Gelometer Reading	pH of Jelly
Grams	*Cc.*		
1.4	2.0	22.3	2.96
1.8	2.2	37.8	2.97
2.2	2.4	58.0	2.99
2.6	2.6	81.2	3.08

A straight line is obtained by plotting these points logarithmically, as shown in Figure 4, indicating that the logarithm of the strength of apple pectin jelly is directly proportional to the logarithm of the pectin concentration. The average curve for 100-grade apple pectin is shown on the same graph for comparison. At a jelly strength of 50 the following relationship obtains:

$$100 \times \frac{2.6}{2.05} = 127 \text{ grade}$$

Effect of Pectin Concentration on Optimum Acidity

The above method, although workable, is complicated by the necessity of first determining the optimum pH for the particular sample of pectin under observation. A second difficulty became apparent in the comparison of logarithmic graphs prepared from several sets of data on one sample, each varying slightly in the acidity of the jellies. In each case close approximation to a straight line was obtained but the slope of the curve was found to vary with each small change in acidity. Inasmuch as the grade is figured on the basis of amount of pectin to give a jelly strength of 50 the slope of the

curve becomes important when extrapolation from lower values is involved.

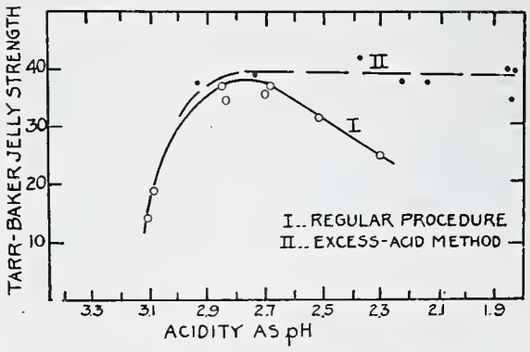

Figure 7. Comparison of Short-Boil and Excess-Acid Methods with Apple Pectin Jellies

The observed variation of slope would be explainable either by the optimum pH varying with increased pectin concentration, or by a variation, with difference in pectin concentration, of the rate at which jelly strength falls off on either side of the optimum. Accordingly acidity-jelly-strength data were obtained for three concentrations of pectin, with all other factors maintained constant, and are shown in Figure 5. Apparently the optimum pH for the highest pectin concentration is about 3.02, while it is close to 2.90 for the lowest concentration. Logarithmic curves plotted from data obtained at pH 2.90 and pH 3.02 are shown in Figure 6. It is evident that appreciable differences in apparent grade might result, depending upon the pectin concentration at which the optimum pH was determined.

Effect of Acid in Preparing Jelly

Bakers' jellies made with commercial apple pectin or pectin concentrates may contain amounts of acid considerably in excess of optimum and yet show excellent jelly strength. Usually these jellies are prepared by pouring a nonacidified pectin-sugar solution into vessels containing the desired acid. Certain advantages of this method have been described by Cole, Cox, and Joseph (*2*). Observations made here indicate that most of the difficulties involved in the routine evaluation of apple pectin jellies may be obviated by the simple expedient of preparing the jelly mixture without acid, adding an excess of acid to the glasses, and pouring the jelly mixture into these at exactly 96° C. Figure 7 shows the close proximation of optimum values obtained by careful adjustment of pH in the standard procedure and those obtained by this excess-acid method over a wide range of pH.

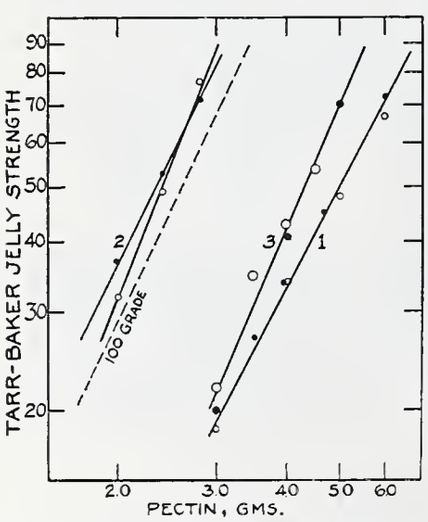

Figure 8. Comparison of Jelly-Strength Values for Apple Pectins

1, Pectin concentrate (Certo), 5.2 grade.
2, Alcohol-precipitated pectin, 108 grade, prepared from destarched and decolorized pomace extracts.
3, Commercial powdered pectin, 61 grade, purchased on open market.
Dots represent data obtained by short-boil method at optimum pH. Circles represent data obtained by excess-acid method. Ten times grams indicated used with sample 1.

Excess-Acid Method

Utensils and jelly glasses used are identical with those described for the testing of citrus pectin.

Two cubic centimeters of 12.5 per cent citric acid are pipetted into each of four glasses. Three hundred grams of sugar are weighed into one 400-cc. beaker and 33 grams into another beaker of the same size. The smaller amount of sugar is moistened with a few drops of water. The desired amount of pectin is thoroughly mixed with the moist sugar and 236 cc. of water are then added. The mixture is stirred to facilitate solution of the pectin. The solution is heated and the sugar added exactly as suggested for citrus pectin. Final net weight is 547 grams of a jelly containing 60 per cent of sugar. After skimming the temperature should be close to 96° C., at which temperature the sirup is poured promptly. Because of the rapid setting the glasses must be skimmed at once. Where a pectin concentrate is used, the same procedure is followed except that the entire amount of sugar may be weighed into the one beaker, and proper adjustment must be made in the amount of water used. If the concentrate contains acid, this must be partially neutralized by the addition of calcium carbonate; the amount used with Certo was 0.14 grams for 50 grams of the concentrate.

Figure 8 and Table II show the excess-acid method applied to the logarithmic evaluation of three apple pectins of very different history. The values obtained by the usual method with careful adjustment of pH are shown for comparison. Judged from its high acid requirement when prepared by the regular short-boil method, sample 3 was quite old.

Table II. Comparison of Jelly-Strength Values Obtained by Short-Boil Optimum pH Method and by Excess-Acid Method, Pouring at 96° C.

Pectin Concentrate (Certo)	Jelly Strength		High-Grade Alcohol Precipitate	Jelly Strength		Commercial Powdered Apple Pectin	Jelly Strength	
	Optimum pH method	Excess acid method		Optimum pH method	Excess acid method		Optimum pH method	Excess acid method
Grams			*Grams*			*Grams*		
30	..	18.5	1.8[a]	30	31	3.0	20	22
35	27	..	2.1[a]	45	46	3.5	..	35
40	34	34	2.4[a]	61	62	4.0	41	43
47	45	..	2.0[b]	37	32	4.5	..	54
50	..	48	2.4[b]	53	49	5.0	70	..
60	73	67	2.8[b]	71	78	...	..	..

[a], [b] Determinations made some time apart by two different operators and using different gelometers.

While it is not claimed that this method will, in all cases, give exactly the same value as that obtained in the usual manner, by careful attention to optimum pH the values will be sufficiently close to serve for most purposes where an estimate of pectin grade or of total jelly units is desired.

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United States Foreign Trade in Nonmetallic Minerals Gains. United States foreign trade in nonmetallic minerals in 1933 showed a substantial improvement over 1932, according to the Minerals Division, Department of Commerce. Export trade increased from $23,470,004 to $30,372,388, or about 29 per cent, while imports showed an upward trend of 19 per cent, being $30,213,675 in 1932 and $36,078,287 in 1933. The 1933 trade was, however, below that for 1929. The 1933 export figure was 42 per cent of 1929, and imports were only 23 per cent of that period. Most of the individual export items in 1933 shared in the upward movement.

A Shearing Disk Plastometer for Unvulcanized Rubber

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A plastometer for unvulcanized rubber is described in which the sample is sheared between the surfaces of a rotating disk and a stationary chamber surrounding the disk. In order to prevent slippage the rubber is kept under a confining pressure and the surfaces which shear it are roughened. The stator chamber is made in two sections which close together under the action of a powerful lever system, and in doing so they automatically cut and form the sample of rubber. A complete plasticity measurement, including heating the sample, can be made in 3 minutes. The measurement obtained, called the shearing viscosity, is proportional to the mean absolute viscosity of the sample.

An IDEAL plastometer for unvulcanized rubber would give a precise measurement of plasticity, would complete a measurement in 30 seconds or less, and would be sufficiently simple in operation to be used by an unskilled mill-hand. In an effort to develop such an instrument, a number of instruments, operating on a variety of different principles, were built and tried out; but none was found that would satisfy all the above criteria.

Precision being considered a matter of primary importance, it was then felt that the only alternative was to develop a plastometer that would be as simple and as quick in operation as it could be and still remain accurate. The shearing plastometer described below was the result.

Shearing Plastometer

Obviously, a quick plasticity measurement requires quick heating of the sample to a standard temperature, which in turn requires that the sample must be small in at least one direction. This obvious fact was taken as the first guiding principle in designing a more satisfactory plastometer; and it appeared most desirable that the sample should have the form of a thin sheet.

The next point to be settled was: What sort of deformation should the sheeted sample be given in measuring its softness or hardness? Compressing the sample to a still thinner sheet did not appear promising, according to previous experiments with certain modifications of the compression type of plastometer. Apparently the only practical alternative was to use a simple shearing deformation with the shearing motion tangent to the bounding surfaces of the sheet. A simple form of apparatus for producing such a deformation is the conventional rotation viscometer in which the test material is contained between a pair of concentric cylinders in relative rotation; or, in an alternate form, the material could be held between a pair of parallel circular disks, one of which is rotated.

Preliminary experiments proved that two conditions are necessary in an instrument of either of the two forms suggested, to produce shearing in a sample of rubber and prevent slipping at the surfaces: (1) The tangentially moving surfaces in contact with the rubber must be sharply corrugated or otherwise roughened, and (2) the rubber must be subjected to a confining pressure which holds it in intimate contact with the roughened surfaces. A simple hydrostatic pressure, supplied, for example, by a pump acting on a liquid, would not suffice for the second requirement. The pressure must be confining in the sense that it is applied directly to the rubber by mechanical means which force and hold the rubber in place and at the same time permit air to escape.

In accordance with the above principles two successful shearing plastometers have been developed, one in the cylindrical form and one in what is essentially the disk form. The cylindrical form is used primarily for research work of a special character. The disk form is used for general plasticity work in both laboratory and factory, and it is this form that is to be described here. Its essential parts are shown in Figure 1.

The roughened surfaces between which the rubber is sheared consist of the disk-shaped rotor, 1, and the upper and lower halves of the stator, 2 and 3. The two halves of the stator have the shape of shallow circular cups, and, when held with their brims in contact, form together a closed cylindrical chamber. The rotor is held vertically centered in the stator chamber by means of a shoulder on the rotor shaft and by the pin, 4, in the center of the chamber roof. The top and bottom surfaces of both rotor and stator are covered with a rectangular array of sharp points, produced by cross-hatching the surface with shallow V-shaped grooves. The sides of both rotor and stator are similarly covered with sharp ridges, produced by a series of longitudinal V-cuts. The device for maintaining pressure on the rubber consists of the pair of plungers, 5 and 6, forced downwards by springs 7 and 8.

The shaft of the rotor, extending through a hole in the floor of the stator chamber, fits into the spindle, 9, and is slotted to receive the key, 10, in the spindle. The spindle carries the worm gear, 11, which engages with the worm, 12, mounted on horizontal shaft 13. The spur gear, 14, mounted on the end of shaft 13, engages with a pinion on the shaft of a synchronous alternating current motor not shown in the figure. Shaft 13 is free to move longitudinally in its bearings, as well as to rotate, but its horizontal travel is opposed by the leaf spring, 15, supported in clamp 16. The horizontal travel of the shaft, which is equal to the deflection of the spring, is indicated by the micrometer gage, 17. The upper and lower platens, 18 and 19, can be heated by either steam or electricity; and each platen has a thermometer hole for measuring the temperature in the center of the platen. The upper platen can be moved vertically by means of a double lever system operating through the connecting rod, 20. One of the two levers gives a relatively large travel and low mechanical advantage. The other lever gives a small travel and an enormous mechanical advantage in the position where the two halves of the stator chamber are closing together.

The dimensions of the rotor and stator are as follows: diameter of rotor, 3.810 cm. (1.5 inches); diameter of stator, 5.080 cm. (2.0 inches); thickness of rotor, 0.554 cm. (0.218 inch); depth of stator chamber, 1.062 cm. (0.418 inch).

The speed of the rotor is 2 revolutions per minute. The pressure exerted by plungers 5 and 6 is 30 to 60 kg. per sq. cm. (400 to 800 pounds per square inch). Any deviations from the standard frequency in the alternating current supply to the synchronous motor would cause corresponding deviations from the standard speed of the rotor; but the frequency control in modern electric generators is generally quite accurate enough for the shearing plastometer. The temperature adopted as standard for plasticity measurements is 100° C. Spring 15 is adjusted in clamp 16 so as to give a gage reading of 100 under a force of 18,144 grams (40 pounds) while the plastometer is running empty. During calibration

this force is produced by a weight attached temporarily to the spring.

Operation

When the upper platen is raised the rotor and shaft can be lifted out. The rotor disk and the inside of the stator are brushed with a soap solution to prevent excessive sticking of the rubber. After the soap has dried a slab of rubber is

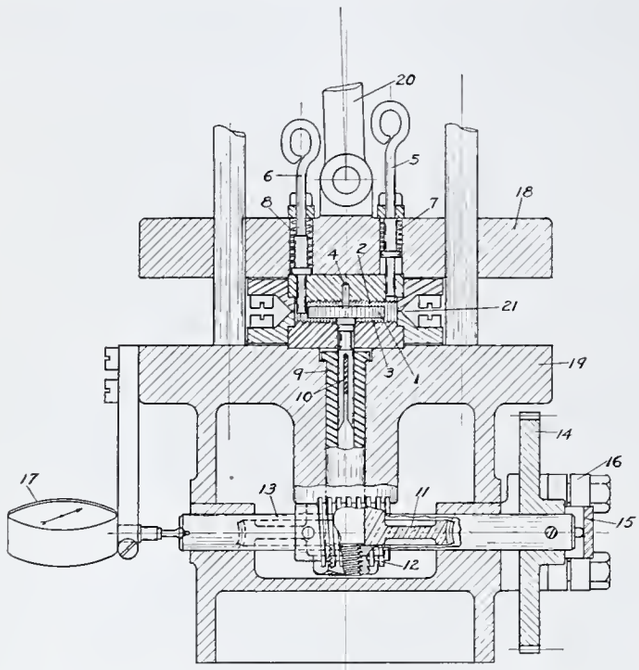

Figure 1. Diagram of Plastometer

placed above and below the rotor, the lower slab being pierced or cut to receive the rotor shaft. The rotor is placed in position and the plastometer closed. During the later stage of the closing operation the excess rubber is forced out between the approaching edges of the chamber, at 21. The rubber resists this forced flow through a narrowing space and consequently builds up a back pressure within the chamber which forces up plungers 5 and 6. After the plastometer is closed the rubber is allowed to warm up for a period of 1 minute. The motor is then turned on. As the rotor begins to turn in the rubber, thereby shearing it, the rubber exerts an opposing torque on the rotor, which in turn transmits a horizontal thrust to shaft 13. This thrust causes the shaft to push against spring 15, thereby deflecting it; and the deflection is registered by gage 17. Because of the thixotropy of the rubber, as explained later, the gage reading goes through a maximum during the first 2 or 3 seconds and then begins to fall. If there is no air in the sample, the gage reading falls asymptotically to a value which remains constant except for small, irregular fluctuations of about 1 per cent. If appreciable quantities of air are enclosed in or with the sample, the gage reading will pass through a minimum while the air is being worked out of the rubber by the shearing action. Plungers 5 and 6, pressing continuously on the rubber, finally compact it; and the reading rises asymptotically to a constant value. In either case, whether there is air in the sample or not, the reading generally reaches a substantially constant value within 1 minute after the motor is turned on. This constant gage reading is proportional to the stiffness or the viscosity of the rubber and is called its "shearing viscosity."

A sample initially at room temperature cannot be heated to a uniform temperature in 1 minute, but the sample is hot enough at this time to permit turning on the motor; and by the time the final reading is taken the temperature is essentially uniform.

For most rubbers and compounded stocks the total time required to soap the plastometer, insert the sample, heat it, take the reading, and remove the sample is 3 minutes. With certain samples, particularly unbroken rubber or cold tread stock not recently milled, more time may be required because the gage reading then takes longer—from 3 to 5 minutes—to reach a constant value. If hot samples are taken direct from a mill, the time required to complete a measurement can be considerably reduced. In a certain series of laboratory experiments, thirty-six samples were measured in 44 minutes, or at the rate of one in 1.25 minutes.

The factory shearing plastometer is not equipped to measure the elastic recovery of the sample after deformation. An accessory device could undoubtedly be added to make this measurement possible; but so far the measurement has not seemed of sufficient importance to justify the additional complication.

Advantages and Disadvantages

The major advantage of the shearing plastometer,[1] its speed, is obvious from the description of its operation.

Another advantage, not quite so obvious, is that from two to six samples, properly cut and placed in the plastometer, can be measured simultaneously to give a single average reading. Thus, even if a batch of rubber is not homogeneous, a good determination of its average viscosity can be made with a single measurement.

In accuracy or sensitivity the shearing plastometer compares favorably with the Williams form of the compression plastometer. The comparison was made by making five or more check measurements with each instrument on each of a series of two or more samples.

The shearing plastometer is not as simple or as inexpensive as could be desired; but it requires no oven and no equipment for preparing samples, and on the whole it is no more expensive than other types of plastometers with their necessary accessories.

Certain advantages of the shearing plastometer are inherent in its action on the sample. The ability of the plastometer to work air out of the sample has been mentioned. Another result of continuously working the sample during the measurement is that the sample is measured in its more plastic state, as opposed to the harder condition that it attains when allowed to rest. For example, if a sample of rubber is sheared in the plastometer till it gives a constant reading, is allowed to rest a minute or two and is then sheared some more, the gage reading again goes through a maximum in the second shearing period, when there can be no question of temperature lag or trapped air. The phenomenon is due to the thixotropy of the rubber, or the property of softening while being worked and hardening again while standing. It is because of thixotropy that, in order to obtain smooth calendering, rubber must be not only warmed but also worked, or plasticized, immediately before calendering. Since those forming operations in which plasticity is important are quite generally carried out with the rubber in the plastic or softened

[1] A plastometer of the shearing type has been developed by Naylor (*3*). In Naylor's instrument the stator was a shallow cylindrical cup with roughened bottom and smooth sides, and the rotor was a roughened disk which fitted inside the cup. The pressure required to prevent slippage was produced by weights which were supported on the rotor shaft and pressed the rotor into the cup. The present instrument is different from Naylor's in three important respects: (1) The sample is automatically formed to fixed dimensions by the plastometer itself as it is closed, (2) the pressure is maintained without any change in the relative position of rotor and stator when rubber leaks out of the chamber, and (3) the effect of friction between rotor and stator is greatly reduced by making the contacting surfaces of rotor and stator small in comparison with the rotor itself.

condition, it naturally seems preferable to measure its plasticity in that condition.

The main disadvantages of the shearing plastometer arise from the fact that it is a machine, as well as an instrument, and therefore subject to wear. The rotor has been the most troublesome part so far. Its roughened surface is worn smooth by the tool, a brass-tipped screw driver, used to lift it out of the chamber when a measurement is completed.

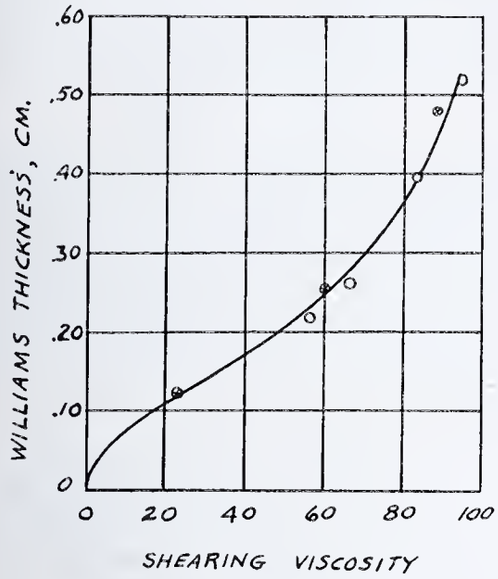

Figure 2. Relationship between Shearing Viscosity and Williams Plasticity

Also, if the rotor shaft becomes slightly bent, it binds against the sides of the hole in the floor of the chamber. The material originally used for the rotors was chrome-vanadium steel, which was chosen to give the necessary strength in the shaft. However, experience has shown that hardness in the rotor is just as important as ultimate strength. The plastometers are now equipped with rotors of case-hardened carbon steel, and these are wearing much better than did the chrome-vanadium rotors.

In the beginning it was feared there might be difficulty with rubber sticking in the corrugations of the rotor and stator. On the whole, however, this has not been the case; and the entire plastometer, including the chamber, pressure reservoirs, and the space under the chamber, can be kept clean without much trouble.

Results Obtained

The shearing plastometer gives results which in general do not differ in their indications from those obtained with other plastometers—that is, a series of samples arranged according to softness by the Williams plastometer (*6*), for example, will usually be arranged in the same general order by the shearing plastometer.

Figure 2 shows quantitatively the relationship between the shearing viscosity and Williams plasticity, which is the thickness of a 2-cc. sample after 3 minutes' compression under a 5-kg. load at 100° C. In the present case the Williams samples were weighed to the required volume on the assumption that the density was 0.92. The points on the curve represent two different batches from two different lots of smoked sheet broken down on a laboratory mill, samples being taken off during the milling. The highest readings represent unbroken rubber; the lowest represent "dead milled" rubber of a plasticity suitable for making cements. The plasticity measurements were made between 1 and 2 days after milling. The curve in Figure 2 is drawn tangent to the ordinate axis at the origin because, according to theory, the viscosity is proportional to the final thickness in the Williams plastometer, raised to some power higher than the first (*1, 4, 5*). It is shown below that the shearing viscosity is proportional to the mean absolute viscosity.

It should not be assumed from these results that the agreement between the two instruments is always so close. When measurements on samples of different kinds of rubber or on compounded stocks are compared, considerable scattering from the curve of Figure 2 is observed. Nevertheless, those who are accustomed to thinking in terms of Williams plasticities can use Figure 2 as a rough guide in interpreting shearing viscosities.

In Figure 3 are shown the shearing viscosities of three samples of smoked sheet at temperatures from 70° to 115° C. The positive temperature coefficient of viscosity in sample *A* at the higher temperatures is remarkable; but this peculiar behavior of unbroken or slightly broken rubber is verified by measurements made with the cylindrical plastometer. It appears plausible that, at these temperatures and rates of shear, crude rubber is not truly plastic. Extensive deformation is probably accompanied by a complicated combination of shearing and tearing actions within the rubber.

Theory of Shearing Plastometer

The shearing plastometer, like most other plastometers for rubber, really measures the softness or hardness, or, if we like, the viscosity of the rubber. The gage reading, or shearing viscosity, is proportional to the true mean viscosity of the sample.

The factor of proportionality, or conversion factor, depends upon the dimensions and other details of the plastometer. We proceed to derive this conversion factor theoretically and to test it with measurements made with both the cylinder and the disk plastometers on the same rubber. We need not correct for the space in the rubber occupied by the top of the rotor shaft and pin 14; for the rate of shear in the rubber and the moment arm about the axis of the rotor are both very small in these regions. The total torque on the rotor

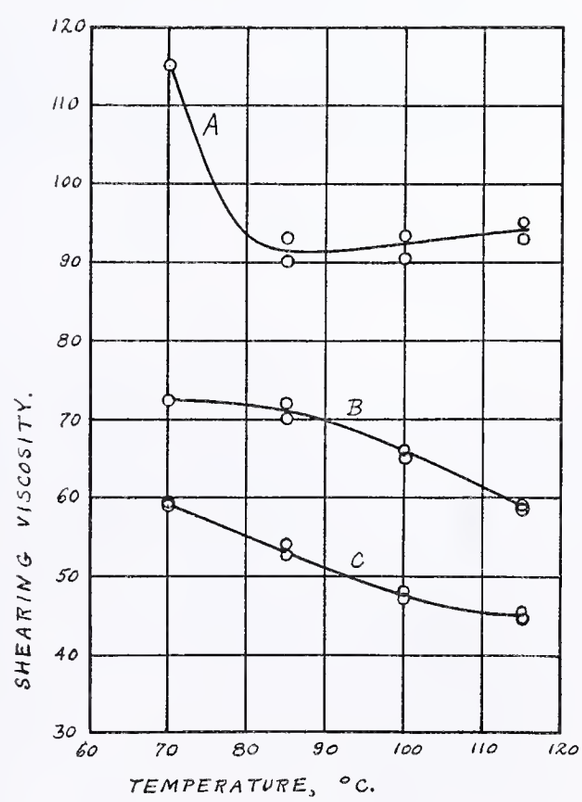

Figure 3. Shearing Viscosities of Smoked Sheet

A, crude smoked sheet *B*, milled smoked sheet
C, milled smoked sheet

resulting from the viscous resistance of the rubber is then given by

$$T = 2\int_0^R \eta(r) \times \frac{r\Omega}{a} \times r \times 2\pi\, rdr + \eta(s) \times \frac{R\Omega}{b} \times R \times 2\pi Rh \quad (1)$$

in which T = torque acting on the rotor
r = radial distance from the axis of the rotor
R = radius of the rotor
h = thickness of the rotor
a = vertical clearance between rotor and stator above or below the rotor
b = effective radial clearance between rotor and stator
Ω = angular velocity of the rotor in radians per second
$\eta(r)$ = viscosity of the rubber at the rate of shear prevalent above or below the rotor at the distance r
$\eta(s)$ = viscosity of the rubber at the rate of shear prevalent at the side of the rotor

All quantities are to be expressed in c. g. s. units. The various factors separated by the $\times$'s in the two right terms of Equation 1 are, in order, viscosity $\times$ rate of shear $\times$ moment arm $\times$ area. The product of the first two factors gives the shearing force per unit area, by the definition of the coefficient of viscosity.

As has been stated, spring 15 on the plastometer is adjusted to give a gage reading of 100 under a force of 18,144 grams. Therefore between the gage reading and the torque we have the relation

$$T = \frac{G}{100} \times 18{,}144 \times g \times P \quad (2)$$

in which G = gage reading
g = gravitational acceleration
P = pitch radius of worm gear 11
= 5.08 cm. (2 inches)

From Equations 1 and 2,

$$G = \frac{1}{181.44\, gP}\left[\frac{4\pi\Omega}{a}\int_0^R \eta(r)r^3dr + \frac{2\pi hR^3\Omega}{b}\eta(s)\right] \quad (3)$$

We now define η_m, the mean viscosity of a sample, as that constant viscosity which an imaginary sample must have to give the same reading in the shearing plastometer as the real sample. Then according to Equation 3 we must have

$$G = \frac{\eta_m}{181.44\, gP}\left[\frac{4\pi\Omega}{a}\int_0^R r^3dr + \frac{2\pi hR^3\Omega}{b}\right] \quad (4)$$

The integral in this equation can now be evaluated, but we must consider also the value of b, the effective radial clearance between rotor and stator. The effective clearance in any region is the distance between rotor and stator along a path which at each point is normal to the surface of principal shear in the rubber. Starting from the corner of the rotor, this distance is a. From a point on the side of the rotor at a distance a from the corner, the effective distance to the stator is $2a$ or a little more. Therefore, we take $3a/2$, or 0.381 cm., as the mean effective clearance between rotor and stator as applied to that portion of the side of the rotor which is within the distance a from a corner. For the central region on the side of the rotor, which is only a narrow strip in the present design, we take the effective clearance to be the radial clearance between rotor and stator, or 0.634 cm. The mean effective clearance is the mean of these two values when weighted in proportion to the respective areas to which they individually apply. Thus, approximately

$$b = 0.400 \text{ cm.}$$

Now integrating and substituting numerical values in Equation 4 we find

$$\eta_m = 1.933 \times 10^4\, G \quad (5)$$

and 1.933×10^4 is the theoretical conversion factor for calculating mean viscosity from shearing viscosity.

But by eliminating G and T from Equations 1, 2, and 4, we obtain also

$$\eta_m = \frac{\frac{4\pi\Omega}{a}\int_0^R \eta(r)r^3dr + \frac{2\pi hR^3\Omega}{b}\eta(s)}{\frac{4\pi\Omega}{a}\int_0^R r^3dr + \frac{2\pi hR^3\Omega}{b}} \quad (6)$$

Now if the functional relation between η and the rate of shear has been determined for a particular sample of rubber by measurements in the cylinder plastometer, and if the shearing viscosity, or G, has been determined for the same rubber by a measurement in the disk plastometer, we can then calculate from Equations 5 and 6 two different values of η_m for comparison. This is equivalent to comparing a measured value of G with a value calculated from Equation 3 by means of values of η determined with the cylinder plastometer.

The absolute viscosities of rubber at different rates of shear can be calculated from measurements with the cylinder plastometer by means of equations that have been published elsewhere (*2*). The relationships found between the viscosity of rubber and the rate of shear are not at all simple. The maximum rate of shear in the disk plastometer, calculated by setting $r = 1.905$ in Equation 8 below, is 1.6 radians per second. For this and somewhat lower rates of shear it was found that the viscosity of a certain sample of slightly milled smoked sheet is approximately represented by the equation

$$\eta = 12.6 \times 10^5\, \omega^{-5/7} \quad (7)$$

in which ω is the angular rate of shear in the rubber, expressed in radians per second.

Now, as indicated in connection with Equation 1, the rate of shear above and below the rotor of the disk plastometer is

$$\omega(r) = \frac{r\Omega}{a} \quad (8)$$

and at the side,

$$\omega(s) = \frac{R\Omega}{b} \quad (9)$$

By means of Equations 7, 8, and 9, η_m in Equation 6 can now be evaluated entirely in terms of the constants of the plastometer and the parameters in Equation 7. We thus find

$$\eta_m = 1.15 \times 10^6 \text{ poises} \quad (10)$$

The measured value of G for this particular sample of rubber was 66.5. Hence from Equation 4,

$$\eta_m = 1.28 \times 10^6 \text{ poises} \quad (11)$$

In the case of a softer sample of smoked sheet, for which the viscosity found by the cylinder plastometer was

$$\eta = 6.67 \times 10^5 \times \omega^{-2/3} \quad (7a)$$

and the shearing viscosity, or G, was 38.5, the mean viscosities calculated according to Equations 5 and 6 were, respectively,

$$\eta_m = 0.624 \times 10^6 \text{ poises} \quad (10a)$$
$$\eta_m = 0.745 \times 10^6 \text{ poises} \quad (11a)$$

For either the hard or the soft sample of rubber there is rough agreement between the two values of the calculated mean viscosity, η_m. We are justified in concluding, therefore, that the analysis of the disk plastometer that has been presented is approximately correct and, further, that the shearing viscosity, determined by the disk plastometer, is approximately proportional to the true mean viscosity of the sample. If the cylinder plastometer can be accepted as a standard, absolute instrument, the check results reported above indicate that the conversion factor defined by Equation 5 is about 14 per cent too high. A better value is given by

$$\eta_m = 1.7 \times 10^4 G$$

The discrepancy of 14 per cent can be partially but not completely explained as being due to certain corrections which should be made. The deflection of the spring in the disk plastometer is not strictly proportional to the load and is 2 or 3 per cent too high at the readings found for the two check samples discussed above. Furthermore, the friction in the disk plastometer was found to reduce the gage reading by 5 per cent, whereas in the cylinder plastometer the friction correction is only 2 per cent or less. The friction in the disk plastometer was determined by applying a known torque to the rotor head, by means of a pair of weights and pulleys, while the motor was running.

Acknowledgment

The author takes pleasure in acknowledging many helpful suggestions from R. H. Gerke during the progress of this work. To H. T. Battin and G. Winter credit is due for important mechanical details in the design of the shearing plastometers.

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Removal of Impurities from Methanol

Use of Nessler's Reagent as a Test

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During the course of certain work it was desired to have methanol which gave no test with Nessler's reagent, thereby indicating the absence of aldehydes, acetone, or higher alcohols. The impurities which are stated by the manufacturer as being present in commercial synthetic methanol are acetone (less than 0.1 per cent) and traces of formaldehyde. The common test for the presence of acetone is the formation of a precipitate with mercuric cyanide, a method credited by Hartley and Raikes (*6*) as being sensitive to 0.002 per cent. In place of mercuric cyanide the writers have used Nessler's reagent as advised by Gross (*5*). Under the conditions herein described this reagent is sensitive to six parts in a million (0.0006 per cent).

As a chemical method to insure the removal of any possible trace of acetone the writers have employed the formation of a resin (*9*) by reaction with furfural in the presence of an alkali rather than the familiar use of sodium hypoiodite (*1*, *6*), sodium hypochlorite (*8*), or calcium hypochlorite (*4*) since the reagents are more economical than the hypoiodite and the dilution with water is much less. By refluxing methanol with furfural and aqueous sodium hydroxide and distilling through a fractionating column, a yield of 95 per cent of methanol which gave no test with Nessler's reagent was obtained. To demonstrate the completeness of this method for the removal of any acetone which may be present, acetone was added to the alcohol in the experiments described below.

Removal of Acetone

The reaction was carried out by adding 25 cc. of furfural and 60 cc. of 10 per cent sodium hydroxide solution to 500 cc. of methanol containing 1 per cent of acetone. After refluxing on a steam bath overnight, a Davis fractionating column (*3*) of twenty turns, previously silvered and evacuated according to the directions of Scott, Cook, and Brickwedde (*11*), was attached and the alcohol distilled from a water bath. The first fraction, consisting of 3 or 4 cc., had a trace of formaldehyde present as shown by a dark precipitate when tested with Nessler's reagent. The second fraction contained 475 cc. (95 per cent of the original methanol), boiled between 64.5° and 64.6° (corrected) at 756 mm., and showed no cloudiness with Nessler's reagent.

When quantities of water much smaller than those given above were used in the purification, the resin resulting was harder and stuck to the flask, requiring the use of acetone as a solvent. Less efficient fractionation or the use of a free flame gave a lower yield due to the necessity of rejecting a greater portion at the end of the process when water containing traces of furfural was carried over. The use of a good column has already been advised by Jones and Amstell (*7*) for the preparation of anhydrous alcohol.

The process was successfully applied to methanol containing 5 per cent of acetone by using proportionately greater quantities of reagents.

Test for Acetone

Nessler's reagent was prepared by adding 18 cc. of an alkali solution (270 grams of sodium hydroxide diluted in water to 1 liter) to 30 cc. of a potassium iodide–mercuric chloride solution (36 grams of potassium iodide and 13.6 grams of mercuric chloride diluted in water to 500 cc.) and shaking. A small quantity, 2 cc., of the distillate was added to 2 cc. of this reagent in a small test tube. A white turbidity resulted in a few seconds if 0.0006 per cent or more of acetone were present. With a higher percentage, about 0.011, a yellowish white voluminous precipitate formed. With a still larger quantity of acetone, about 0.5 per cent, the precipitate was dissolved. Owing to this solubility of the precipitate it is necessary to make a preliminary test by adding 1 drop of the distillate to 2 cc. of the reagent. The range of this test is from 0.1 to 50 per cent of acetone. Smaller aliquot portions of the distillate and Nessler's reagent have been used successfully in the test.

If a trace of furfural were present the turbidity had a brownish tinge, which is characteristic of the behavior of the reagent with aldehydes. According to Gross (*5*), alcohols higher in the series than methanol and secondary alcohols will also form a precipitate.

Test for Furfural

Because of the volatility of furfural in steam (*2*) and the danger of its being carried over in the end portions, a specific test for this aldehyde was desirable. When 6 to 8 drops of the distillate were added to 0.25 cc. of an aniline acetate solution (3 cc. of freshly distilled aniline in 2 cc. of glacial acetic acid) a pink color occurred if furfural were present. The test was found to be sensitive to 0.0001 per cent of furfural. Mueller (*10*) states that the test is accurate to 0.0005 per cent.

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Preparation of Microscopic Glass Spheres

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In certain physico-chemical researches, as in the study of rates of diffusion of gases and liquids and of solids in gases or liquids, it is desirable to have perfect spherical particles of known size and weight. Calculations are simplified since spheres are regular-shaped bodies, whose physical constants are readily determined, and will pack in a regular geometric pattern leaving interstices whose dimensions are calculable. Glass lends itself readily to the purpose. A given glass is uniform in composition. Its specific gravity and hence its weight may be determined if its size can be measured.

After a careful analysis of the problem, a procedure for the preparation of microscopic glass spheres suggested itself. It was necessary to subject each fine particle of glass, insulated from every other particle, to a temperature sufficiently high to insure its becoming a free-flowing liquid. At the same time the particle had to be kept in free suspension, until it became solid enough not to change its shape on contact with other bodies. Air would insulate the particles from each other, and at the same time permit them to be heated until they were free-flowing. It would keep them in suspension, if it were moving rapidly enough, and allow them to cool to rigidity before touching anything.

Apparatus

The apparatus designed by the author utilized such materials as were available and could be constructed at the minimum cost and effort.

A system was constructed (*A*, Figure 1), utilizing a wind turbine with a hollow shaft to churn the powdered glass while a powerful stream of compressed air descended the shaft and was forced to pick up the glass powder which was inclosed in a bottle having the turbine sealed in it. A glass tube led from the bottle to the next piece of apparatus, *B*, consisting of a blast lamp, the air side of which connected to the outlet from the bottle containing the powdered glass. Gas from the main was fed to the other inlet of the burner. This blast lamp was placed at one end of a clay-graphite cylinder, *C*, 6 inches in diameter, 3 feet long, and 1 inch thick. Two blast lamps entered tangentially, facing forward at a slight angle, so that their flame would swirl and at the same time shoot forward down the cylinder. This kept the flames from one burner impinging on the second. Gas for these two burners was supplied by interposing a blower between the gas main and the burner outlets. A Y-tube supplied the necessary connections.

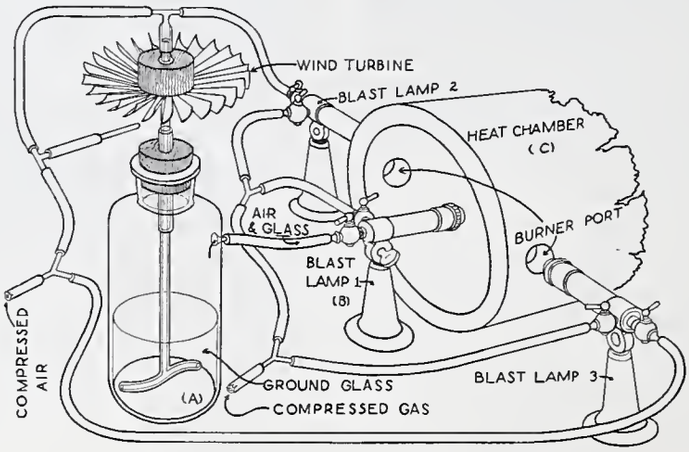


Figure 1. Detail of Apparatus

Following the heat chamber was the settling chamber (*D*, Figure 2), consisting of a horizontal metal pipe 3 feet in diameter and 10 feet long, open at both ends, fitted on the far end into a cardboard box 6 feet square, *E*. The box had small holes punched in the top to allow the escape of air. The bottom of the pipe and box were lined with black paper in order that the glass spheres might be discernible after they had settled. The pipe had a door fastened on the side to allow easy access, and the box was so arranged that a flap could be opened to get inside. The heat chamber exit was placed near the top of the settling chamber entrance in order that the molten glass particles might travel further before settling.

After assembling the apparatus, a run was made. The gas cocks were opened to lamps 2 and 3 and the blower started. The compressed air was turned on and the burners adjusted for maximum temperature and optimum position. The heat chamber was warmed to white heat. The wind turbine was then set in motion and adjusted to maximum speed. The gas was turned on in burner 1, and the compressed air released down the hollow turbine shaft. The air supply was carefully adjusted so that little glass powder was picked up and carried into the heat chamber.

By varying the speed of the turbine and the air pressure down the shaft, it was possible to control

the amount of glass passing through the heat chamber and also the speed as it was carried along by the wind stream.

The apparatus was run in half-hour periods and the glass spheres were collected from the black paper lining where they had settled. The larger balls were, of course, nearer the heat chamber, while the smaller were at the farther end of the box. Some were even on the sides and top inside of the box, where they had floated on the air stream.

Examination under the microscope gave the size range from 0.01 to 0.00001 inch. There were about 95 per cent perfect spheres, about 4 per cent egg-shaped particles, and about 1 per cent deformed particles among the larger sizes. The percentage of perfect spheres increased in the finer sizes, until the very smallest were all perfectly spherical in shape. From any given section of the settling chamber the particle size varied very little. A re-run of the larger sizes would probably bring the percentage of perfect spheres nearer 100.

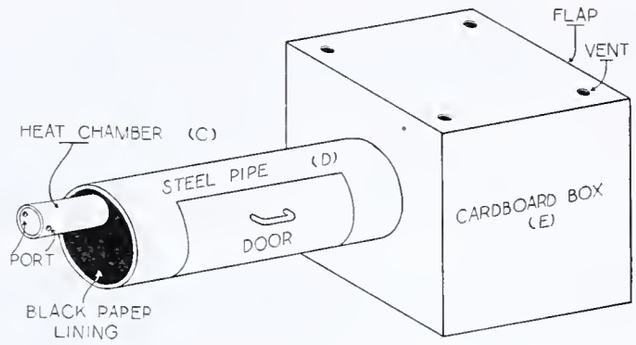


Figure 2. Settling Unit

Uses of Spheres

Aside from the uses mentioned above, the following have been suggested:

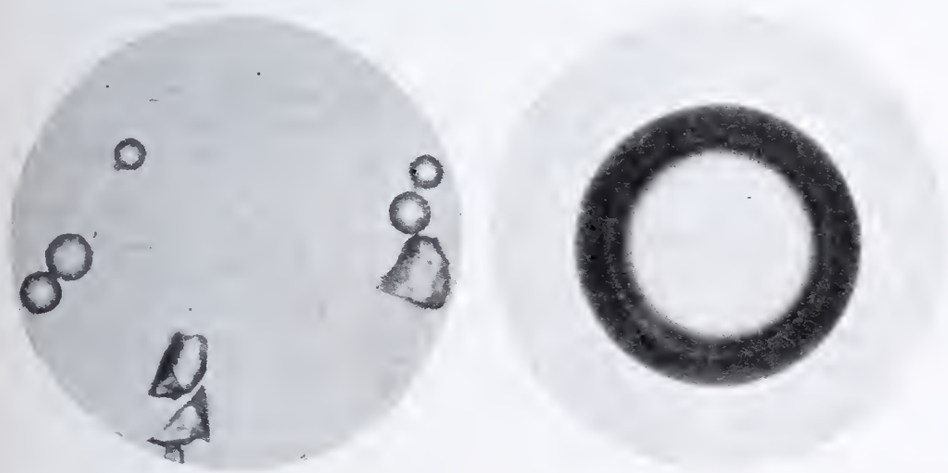
1. In the preparation of porous plugs or filters for use in a study of such problems as (*a*) the recovery of petroleum from underground sand deposits by displacement with water, aqueous solutions, gases, etc. (*1*); (*b*) diffusion of gases in long columns where major eddy currents could be prevented by a packing of uniformly small spheres; (*c*) the filtration of liquids, destructive to ordinary filtering media; (*d*) filtration problems where filter cakes of material having a known uniform size are desired, etc.

2. In studies of sedimentation phenomena such as rate of settling, settling equilibria, Brownian movement, etc., or where uniformly sized spherical particles would be an adjunct to lecture demonstration or instruction.

3. In studies of certain adsorption phenomena where large surfaces of known value are desired.

4. In studies of fluid flow where stable suspensions of solid spherical particles having a different index of refraction from the fluid under consideration would permit fluid movement to be observed, etc.

With a large enough settling chamber so arranged that eddy currents were eliminated, no trouble should be entertained in obtaining a size separation of particles by settling. A wider and longer heat chamber would lengthen the time of heating and permit incompletely converted particles to be converted to spheres. The wind turbine mixer and the glass-air jet could be redesigned for greater efficiency. Continued experimentation would determine the optimum conditions and apparatus.



1, Partial conversion. Poor conversion from ground to spherical glass takes place when the particles are shot at too high speed through heat chamber. Close examination will reveal very tiny particles in close contact with spheres. These particles are not round and seem to adhere through electrical charge. They can be removed by careful manipulation with a glass hair under the microscope. (1323 diameters)

2, Diffraction pattern. Conclusive evidence of spherical shape of particle. Diffraction pattern and outer edge are both perfectly circular under the microscope. This particle presented a beautiful display of colored rings, unreproducible in photograph. Close examination will reveal two bright rings and possibly a third in the dark band. (5418 diameters. Original 0.00066 cm.)

Figure 3. Photomicrographs of Glass Spheres

Photographic Data

The illustrations for this article were made on Press 2000 plates, triple emulsion, the exposures running from 15 to 30 seconds with a 60-watt source of light brought to a focus with a plane mirror and a substage condenser. The plates were developed under red light in Eastman D11 contrast developer for 7 minutes, fixed, and washed. The positives were printed on Azo paper with D72 developer.

Because of the inadequacy of photographic apparatus and technic, it was impossible to photomicrograph the very small particles, some of which were a small fraction of the size of that shown in Figure 3.

Acknowledgment

The apparatus was collected and the experiments were done in the laboratory at Nichols Chemistry Building at New York University, where the research was done under the direction of H. J. Masson, to whom the author feels greatly indebted.

The author is especially indebted to Arthur Liebers for assistance in editing this article, to C. C. Clark for the loan of apparatus which made possible the illustrations, and to Robert Irving Langer for the sketches of the apparatus.

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Flexible Glass. A flexible form of plate glass, produced by a secret process in one of the largest glass factories in Great Britain, is claimed to be meeting with considerable success, according to a report made public by the Commerce Department.

The new glass is flexible to a remarkable degree, and capable of withstanding enormous pressure. In a recent demonstration, a plate of the glass measuring 3 feet in length was raised on two narrow boards. Pressure was then applied, causing the glass to curve, but upon removal of the pressure the glass resumed its normal straightness.

Preparation of Sintered Pyrex Glass Filters

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THE advantages of filters made from sintered glass disks are well known, largely because of the wide use of such filters constructed from Jena glass. The practical difficulties of incorporating Jena filters into general apparatus, which in this country is rarely made from Jena glass, have long indicated the desirability of using Pyrex brand glass. Methods for constructing such filters have been very briefly described by Bruce and Bent (*1*) and by Shatenshtein (*4*), and other workers (*5*) have recorded the construction of filters from Pyrex glass but have not given their methods. Thomas (*5*) and Prausnitz (*3*) have detailed various special uses for sintered glass filters. However, no careful study of the method of making the sintered disk is given, nor are methods recorded in sufficient detail to enable the investigator to prepare at will any desired size or porosity of filter. On this account, this study has been made and it has been found possible to prepare sizes from about 0.375 to 2 inches (0.94 to 5 cm.) diameter or larger, in any desired porosity and without undue chance of failure.

Method

Ground glass of uniform sized particles and of graded sizes is necessary if reproducibility of porosity is to be obtained. Moreover, it is essential that the glass used be reasonably uniform in quality, preferably of the same lot as the tubing into which the sintered disks are to be sealed, in order to have a minimum of breakage. While it is probably not necessary to use glass of the same lot for the disk and the tube into which it is sealed, scrap Pyrex glass from broken apparatus, even though it be thoroughly cleaned, does not seal well into new tubing. This may be a phenomenon of aging of the glass, such as devitrification.

The glass must not be ground in a porcelain or glass mortar, unless the mortar is of Pyrex glass. An iron mortar and pestle were used in this study. The glass is ground and sifted rapidly through a 100-mesh sieve, the coarse particles being reground until a considerable amount of sifted glass is available. This contains considerable iron and some material insoluble in strong acids, presumably iron carbide. The glass is treated with strong acid and warmed to dissolve the iron. The insoluble material will usually float or at least settle more slowly than the main portion of the glass and can be removed by decantation. When the glass cannot be completely cleaned by this treatment, caustic solution instead of acid is applied, and in the rather strong caustic solution the insoluble material can be suspended sufficiently to make decantation possible. The clean glass powder must be graded rather accurately, preferably by use of differential settling rate in an elutriator such as is commonly employed in the separation of different constituents of soils. Grading may also be accomplished by means of a series of sieves of graded fineness. The glass was arbitrarily divided into four grades, as shown in Table I.

Table I. Grading of Glass

Grade	Average Particle Diameter	Approximate Screen Size
	Mm.	*Meshes/inch*
1	0.16	100–150
2	0.08	150–200
3	0.04	200–275
4	0.02	275–325

The glass must now be placed in a mold for sintering. For this purpose the authors have used a mold constructed from brass, because of the ease of obtaining and working this metal, but other metals may be more suitable, since brass invariably discolors the surface of the disk. This discoloration is easily removed by use of carborundum paper after sintering. Bruce and Bent used nickel molds and record no difficulties, though their design is inconvenient and allows only one disk to be made in one mold. The authors' molds were constructed of two brass plates each 3 by 6 inches (7.5 by 15 cm.) The base plates were 0.3125 inch (0.8 cm.) thick and had two upright pins, one at either end, for holding the upper plate which varied in thickness depending on the size of disk being made. The upper plate should be a little thicker than the desired thickness of the disk and should contain a convenient number of holes a little larger than the final size of the disk desired, since the disk shrinks a trifle while being sintered. The upper plate should also have holes corresponding to the pins in the base plate over which it slipped, so that, when assembled the plates are held rigidly together. When paper or Cellophane inserts were placed between the plates to prevent discoloration of the disk by the brass, the carbonaceous material from the paper was mixed with the glass powder and entirely prevented the particles from sintering.

The holes were completely filled with the glass powder, packed as tightly as possible to minimize shrinkage. With grades 1 and 2, simply tapping the mold sharply produced satisfactory settling. With the finer grades, it was necessary to moisten the powder with a few drops of water and pack the wet glass. When this was done the shrinkage was very slight. The water was dried out before placing at sintering temperature to prevent formation of vapor bubbles. While filling the mold, an electric muffle furnace equipped with a pyrometer accurate to ±3° C. was heated. The pyrometer junction was some 2 inches (5 cm.) above the mold in the furnace, thereby registering the temperature of the furnace interior rather than that of the mold. When the temperature reached 800° C., the molds were quickly inserted. The temperature fell off rapidly in all cases until the molds became heated. When the temperature had risen to the correct value for sintering, the rheostat controlling the furnace temperature was manually operated to maintain the sintering temperature as accurately as possible.

Experiments were run to test the effect of time and temperature on the sintering process, and it was found in all cases that a change of a few degrees in temperature had much more effect than even doubling the time. As a result, the standard time chosen for all grades of glass was 15 minutes, since this length of time was not tiresome, and it allowed well for inequalities of temperature, either locally in the furnace or due to lag in the heating elements, both being factors of great importance when temperature control is critical.

The optimum temperatures for the grades of glass used are given in Table II.

At the expiration of 15 minutes at the full sintering temperature, the mold was immediately withdrawn from the furnace and the sintered disks extracted as soon as the mold had cooled sufficiently.

Table II. Optimum Temperatures

Grade	Temperature
	° C.
1	810
2	800
3	790
4	780

Small variations in porosity inevitably occur between individual disks of the same lot, but properly made disks of any one grade invariably differ in porosity from all disks of another grade. Grade 1 is suitable for a rapid filter for coarse precipitates, and is especially adapted to use as a gas bubbler where gases must be scrubbed rapidly. It has been found useful in constructing extractors to retain the solid nonextractives. Grade 4 retained the finest analytical precipitates. Grades 2 and 3 are intermediate in porosity, and are to be recommended for separating analytical precipitates which are not of the very finest varieties, since their speed of filtration is decidedly greater than that of grade 4. Likewise they are suitable for gas bubblers where the volume of absorbent is not large and the gas must be very thoroughly scrubbed in one vessel, as in the quantitative absorption of carbon dioxide in a small volume of alkaline solution. No difficulties have been met in duplicating porosities at various times when the same glass and sintering procedure are used.

All sizes of disks which the authors have made have been successfully sealed into Pyrex tubing. No difficulty has been encountered in the seal itself, but an annular crack in the tube frequently formed at the edge of the smaller sizes of disk on cooling. This difficulty was in no case avoided by annealing with a large flame of any temperature, but could be avoided by sealing the disk into a tapered rather than a straight tube, or better, by using a very fine hot flame to anneal the edge of the seal after partial cooling. The strain is localized at the edge of the seal by contraction of the disk on cooling and the only satisfactory form of annealing is a local application of heat at the point of strain without a reheating of the disk itself. Turning the tube in a lathe and applying pressure at the seal with a carbon rod produced the best seals with a minimum of fusion of the disk. By this procedure the micro external filters described by Kirk (*2*) have been made satisfactorily, though no filters of this small size have been available hitherto.

The authors have used the method of Shatenshtein (*4*) in a few instances. It is successful in sintering Pyrex glass when the size of filter made is small—not over 1 cm. in diameter—and when the glass used is relatively coarse—grades 1 or 2—but the method has very limited application and lacks accurate control and reproducibility.

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A Simple Radio Relay Circuit

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Radio circuits are used in controlling the temperature of both high- and low-temperature thermostats, in the intermittent starting and stopping of motor sets, and in amplifying the current from a photoelectric cell to accomplish these or similar purposes. The advantage of a radio type of relay circuit over that ordinarily used is that, because of the small current in the grid circuit no arcing can take place to foul or disintegrate the contacts. Furthermore, the circuit may be made and broken in an atmosphere containing inflammable vapors (*1–5*).

The principle involved is, that the application of an appropriate voltage (very low amperage is required) to the grid of a suitable radio tube will cause a large decrease in the current flowing in the plate circuit. By having the current in the plate circuit operate a relay, very large currents can be made or broken by appropriate contacts.

The circuits ordinarily described require direct current, and in some cases both direct and alternating current. Since direct current is rarely available, storage or dry cells (B or C batteries) must be used. These are an additional expense and frequently become discharged at a most inopportune time. The writers have adapted a standard single amplifying circuit, which requires only alternating current, for general use in the laboratory. The simplicity of the circuit is immediately apparent from Figure 1.

A is a 171-A power tube which will furnish a plate circuit of approximately 10 milliamperes. *B* is a device for closing the grid circuit. It may be a thermal regulator of the usual mercury type or one made from a bimetallic strip, or it may be a photoelectric cell. *C* is a fixed condenser used to smooth out the intermittent direct plate current and *L* is the source of 110 volts alternating current (60 cycles). M_1 and M_2 are 1- and 2-megohm grid leaks such as are ordinarily found in radios. If the resistor, M_1, is placed between R_1 and *B* the possibility of grounding the source of alternating current is avoided. It also eliminates being shocked while making adjustments. R_1 and R_2 are resistors whose resistances are shown in Table I. If lamps are not used, the resistors should be capable of handling about 50 watts. *T* is a suitable relay. The relays described are manufactured by the Western Electric Company. B59 and 178BY are used by telephone companies on their switchboards and sell for about $4. Relay B59 has only one set of platinum contacts, while 178BY has several. Relay 22A is a large instrument used in communication lines, and has but one contact. The current consumption using relay B59 and two 50-watt carbon lamps in the filament circuit is about 20 watts.

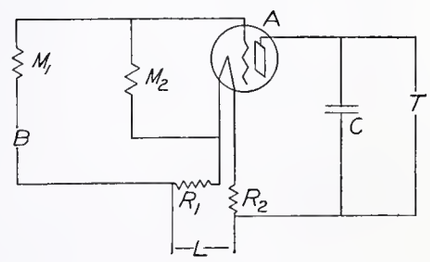

Figure 1

The heavier circuit for operating the apparatus may be closed directly through the operation of the relay contacts, or indirectly by means of a vacuum contact such as those made by the Burgess Battery Company, Chicago, Ill., which will handle 1300 watts at 220 volts, or by means of a mercury switch which may be operated by means of a solenoid con-

nected to the contact points of the relay. Relay 178BY can readily be adapted to operate the vacuum control.

Table I. Suitable Resistances

Relay	R_2 Watts	R_1 Watts	Kind of Lamp	C_1 Mf.	Approximate Plate Current Milliamperes	Resistance of Relay Ohms	Minimum Operating Current Milliamperes
B59	50	60	Carbon	1	2.4	12,000	1.0
	50	50	Carbon	1	1.1		
	50	50	Mazda	1	2.5		
178BY	50	200-ohm variable resistor	Carbon	2	8.5	2000	8.0
	25		Mazda	2			
22A	50	100	Carbon	1 or 2	9.1	100	4.0
	50	50	Mazda	1 or 2	6.0		
	50	60	Carbon	1 or 2	4.0		

This circuit may be used in connection with a photoelectric cell, P. J. 23. The terminals of the cells are connected in the grid circuit at *B*. On being illuminated, sufficient potential is applied to the circuit to produce enough current in the plate circuit to operate the relay.

In order to have the relay operate accurately at regular intervals, the grid circuit may be closed by causing a contact to be made by a mechanism driven by a synchronous motor. An electric clock may be readily converted to a timer by placing contacts on the clock face and closing the circuit through the large hand. If an apparatus is to be started or stopped at a given time, the contacts may be made closed through both hands of the clock. Other possibilities for the use of the circuit will be suggested by the problems in the immediate field of the worker.

Acknowledgment

Acknowledgment is made to R. S. Allison for pertinent suggestions.

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Automatic Vacuum Regulator

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In laboratories having a vacuum supply there is often a need for some device to reduce the degree of vacuum and at the same time maintain it at the desired degree. A vacuum regulator was accordingly designed, similar in principle to that used in commercial regulators, which operates satisfactorily and can be constructed by anyone from ordinary materials.

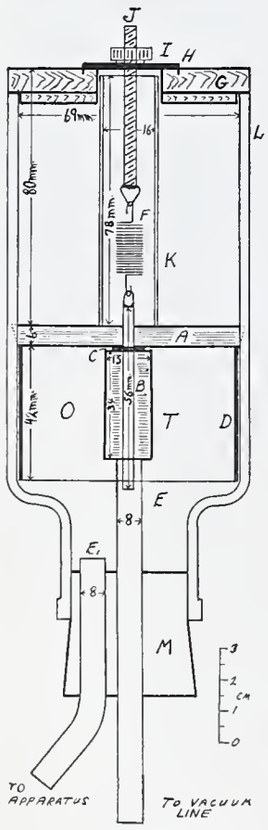

Figure 1. Diagram of Vacuum Regulator

The dimensions as given in Figure 1 need not be rigidly followed and can be modified to fit available materials.

The body, *L*, of the regulator is a wide-mouthed glass bottle, the bottom of which has been cut off and the sharp edges smoothed by rubbing with emery cloth. A rubber disk, *A*, is cut out of an ordinary No. 14 solid rubber stopper, the proper section being selected so that the diameter of *A* is slightly larger than the inside diameter of *L*, thus affording a snug air-tight fit when *A* is placed in position in *L*. A 0.19-inch (0.47-cm.) brass rod, *B*, with a brass washer, *C*, soldered on as indicated and a small loop of wire soldered on one end, is inserted in a 0.125-inch (0.32-cm.) hole which has been cut in the center of disk *A*. A section of 0.125-inch heavy-walled rubber pressure tubing *T*, with ends cut smooth and perpendicular to the hole, is slipped on the lower end of rod *B*.

A sheet of No. 16 Stubs gage (approximately 1.7 mm.) copper is formed into a cylinder, *D*, and slipped into place as shown. The function of this cylinder is to keep the edges of disk *A* in position when suction is applied on the lower side of *A* in chamber *O*. Disk *A* with parts *B* and *T* attached is then put into position. A well-rolled cork, *M*, holding two pieces of glass tubing, *E* and E_1, is inserted in the neck of the bottle, and *E*, with upper end carefully fire-polished, is adjusted so that it just touches rubber section *T*.

Two circular disks of wood, *G*, are glued together and a hole is bored in the center a trifle larger in diameter than the glass tube, *K*. *K* is 2 mm. less in length than the distance between the top of disk *A* and wooden cover *G*. The purpose of *K* is to keep disk *A* from being pulled completely out of position by spring *F* when there is no reduction of pressure in chamber *O*.

A square sheet of copper, *H*, with corners turned down, and a hole in the center to accommodate threaded brass rod *J* and knurled knob *I*, is centered over the hole in the cover *G*. A loop of wire is soldered on the end of *J*, and spring *F*, which is made by winding 16 turns of No. 18 B. & S. gage steel piano wire around a 0.25-inch (0.64-cm.) rod, is put in position. With a spring such as *F* it is possible to vary the degree of vacuum between 1 and 7 inches (2.54 and 17.8 cm.) of mercury. With a stronger spring the range can be extended to the maximum of the vacuum supply.

The operation of the regulator is as follows: With the regulator connected to the vacuum supply and apparatus, knob *I* is turned, placing tension on spring *F*, which pulls disk *A* upward in the center, causing rubber section *T* to be pulled away from tube *E*, allowing chamber *O* and connected apparatus to be evacuated. When the pull of spring *F* is balanced by the pressure of the air on the top of disk *A*, rubber section *T* is pressed against tube *E* and held there until the degree of vacuum in chamber *O* falls off, when spring *F* again pulls *T* away from *E*.

Thus the degree of vacuum is automatically maintained fairly constant in the connected apparatus. The operator by increasing or decreasing the tension of spring *F* can cause a corresponding increase or decrease in the degree of vacuum. A regulator as described has been used very successfully in reducing a line vacuum of 26 inches (66 cm.) of mercury to just a few inches for suction filtering.

Received October, 3, 1933.

Dolomitic Limestone, or dolomite, added to complete fertilizers that are acid-forming in their influence on the soil will prevent them from increasing soil acidity, according to the findings of two U. S. Department of Agriculture chemists, K. C. Beeson and Wm. H. Ross of the Bureau of Chemistry and Soils. This observation is considered especially important for the South where much fertilizer is used.

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Quantitative Spectroscopic Analysis of Solutions

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Calibration curves have been determined for the quantitative spectrographic analysis of columbium, beryllium, titanium, vanadium, tungsten, iron, molybdenum, chromium, lead, and cobalt. These curves are given in both per cent of element and logarithm of the per cent of element present. The average deviation in the determination of samples of known composition was less than 5 per cent of the known concentration.

THROUGH the use of the logarithmic sector method (*1–4*) data have been obtained on the quantitative estimation of columbium, beryllium, titanium, vanadium, tungsten, iron, molybdenum, chromium, lead, and cobalt. Data on a few of these elements (chromium, lead, and cobalt in particular, *5*) have been prepared by other workers, but using different line pairs from those in the present analyses.

The method of analysis follows in general that described by Twyman and Hitchen (*5*) with certain modifications in the apparatus and manipulation. Two different quartz spectrographs were used in this study, a large Hilger (E-185) Littrow spectrograph (linear dispersion 7000 to 2000 Å. = 100 cm., Figure 1-*A*) and a medium Bausch and Lomb Spectrograph, No. 2820 (linear dispersion 7000 to 2000 Å. = 21 cm., Figure 1-*B*). A logarithmic sector (*2, 3*) was used in front of the slits of each of these intruments, actuated by connection with the starter knob of a simple alternating current electric clock. In a modification of the Twyman and Hitchen solution spark apparatus 22-gage copper electrodes were used for both the upper and lower electrodes in place of the previously recommended carbon and gold electrodes. A Pyrex jet was found to be as satisfactory as a quartz jet. The copper lines produced in the spectra (Figure 1) were not objectionable and may reduce to some extent the slight error due to an excess of a foreign anion in the solution to be tested.

The spark was produced by a 20,000-volt 2-kilovolt-ampere transformer. The primary (110 volt) circuit had a resistance in it, to permit the passage of about 1 ampere.

TABLE I. QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SOLUTIONS

Compound Used	Method of Solution	Concentration Range (Element) %	Internal Standard Used	Concentration of Standard *Grams/100 cc. water*	Amount of Standard Added to 100 cc. of Solution *Cc.*	Line Pair Used
Columbic anhydride	K_2CO_3 fusion plus water	0.005 to 1.0	$KMnO_4$	2.8769 (1% Mn)	20	Cb 2927.82 Å. Mn 2933.06
Beryllium sulfate	Water plus 2% H_2SO_4	0.0001 to 0.1	$Bi(NO_3)_3 \cdot 5H_2O$	8.6580 grams $BiO_2CO_3 \cdot {}^1/_2 H_2O$ dissolved in excess conc. HNO_3 and diluted to 100 cc. (3.5% Bi)	50	Be 3131.32 } unresolved Be 3131.97 } Bi 3067.73
Beryllium sulfate	Water plus 2% H_2SO_4	0.0005 to 1.0	$KMnO_4$	2.8769 (1% Mn)	10	Be 2651 (6 unresolved lines) Mn 2939.31
Titanium dioxide	Sodium pyrosulfate fusion plus 5% H_2SO_4	0.005 to 1.0	CrO_3	10.0000 (5.2% Cr)	16.7	Ti 3383.765 Cr 3368.05
Vanadic anhydride	HCl (calculated amount plus 2%)	0.005 to 1.0	CrO_3	19.2308 (10% Cr)	20	V 3093.13 Cr 3118.65 V 3130.270 Cr 3132.053
Tungstic anhydride	NaOH (calculated amount plus 2%)	0.005 to 4.0	$KMnO_4$	2.8769 (1% Mn)	5	W 2589.2 Mn 2593.733
Ferrous ammonium sulfate	Water plus 2% H_2SO_4	0.005 to 1.0	$CoCl_2 \cdot 6H_2O$	16.1424 plus 2% HCl (4% Co)	20	Fe 2382.039 Co 2378.62
Molybdic anhydride	NH_4OH (calculated amount plus 2%)	0.005 to 4.0	$K_2Cr_2O_7$	2.2630 (0.8% Cr)	50	Mo 2848.21 Cr 2849.83
Chromic anhydride	Water	0.005 to 4.0	$NiSO_4 \cdot 7H_2O$	19.1479 plus 2% H_2SO_4 (4% Ni)	10	Cr 3578.687 Ni 3524.543
Lead nitrate	Water plus 2% HNO_3	0.4 to 4.0	$Ni(NO_3)_2 \cdot 6H_2O$	19.9903 plus 2% HNO_3 (4% Ni)	10	Pb 3683.472 Ni 3619.393
Cobalt chloride	Water plus 2% HCl	0.05 to 4.0	$MnCl_2 \cdot 4H_2O$	7.2055 plus 2% HCl (2% Mn)	100	Co 3453.514 Mn 3441.997

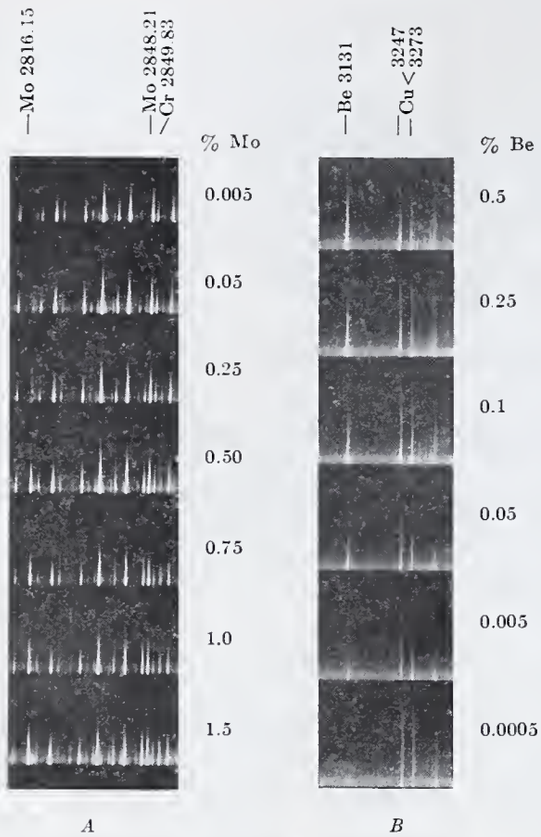

FIGURE 1. SPECTRUM PHOTOGRAPHS

A. Variation of concentration of molybdenum with chromium as internal standard.
B. Variation of concentration of beryllium with manganese as internal standard.

A condenser (0.005 microfarad) was shunted across the secondary terminals of the transformer.

The solutions were prepared by weighing the quantity of pure material required to make a given volume of the most concentrated solutions used and diluting these with distilled water or other indicated solvent to yield the required concentrations. A known amount of the solution of the substance selected for the internal standard was then added to a definite volume of each solution and a photograph made of its spark spectrum. (The photographs were taken on Eastman 33 plates and developed with the Eastman formula D-76 developer with controlled conditions of temperature and time of development.) The lengths of the selected pair of lines were measured with a Bausch and Lomb plate magnifier containing a 20-mm. scale with which the length could be determined to within 0.02 mm. The lines selected for measurement conformed as nearly as possible to the requirements for homologous pairs as described by Gerlach and Schweitzer (*1*). The difference in length of two lines will represent the ratio of their intensities, since by the use of a logarithmic sector the line densities vary at a logarithmic rate. The difference between the length of the line of the standard and the length of the line of the element to be estimated was then plotted against the per cent of the element to be estimated (and also against the logarithm of the per cent of the element to be estimated). These data are presented graphically in Figures 2, 3, and 4. Table I indicates the materials used for examination, the method of solution, the concentration range, and the line pairs measured.

The curves in Figures 2 to 4 may be used as standard or calibration curves in the analysis of unknowns. The procedure in such an analysis is to prepare a solution as indicated in Table I and, if the concentration of the element is approximately known, dilute the solutions to a concentration of approximately that of the center of the calibration curve and photograph its spark spectra. If the concentration is not approximately known, solutions should be prepared by tenfold dilution, so that each solution has one-tenth the concentration of each preceding solution. Three or four such solutions will in nearly all cases cover the desired concentration range. To each solution is then added the indicated amount of solution containing the internal standard and the spark spectrum is photographed. In obtaining these spectra the most dilute solutions should be photographed first and then the more concentrated in the order of their increasing concentration. This procedure reduces the possibility of contamination of dilute solutions with the stronger solutions. The minimum quantity of solution upon which the authors have made observations is about 2 cc. By the use of capillary tubing, however, it should be possible to use micromethods and obtain satisfactory analyses on 0.5 cc. or less. The amount of unknown element in the solution is determined by measuring the lengths of the standard and unknown lines and subtracting the standard from the unknown length; from the calibration curve it can be seen that this difference in length will represent a definite per cent of the element for which the analysis is made.

In Figure 2, the chromium, lead, and cobalt curves are shown together so as to indicate variations in the sensitivity range of the lines chosen for these ele

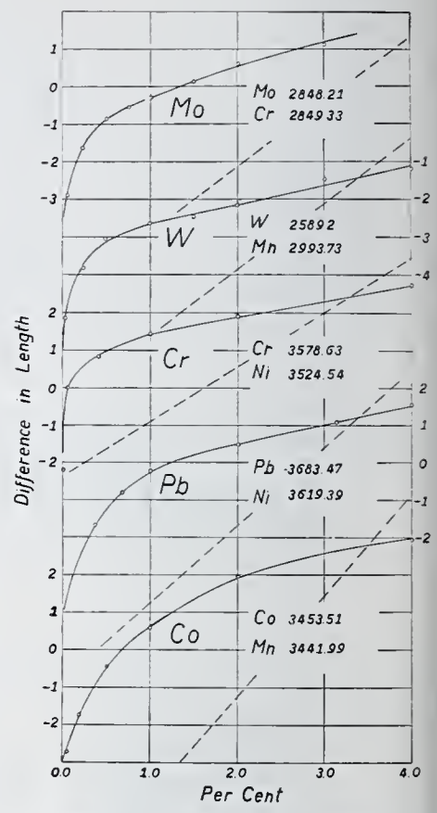

FIGURE 2. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF UNKNOWN ELEMENT FROM DIFFERENCE IN LENGTH OF UNKNOWN AND STANDARD LINES

Dotted lines are logarithm of continuous curves. Slope of logarithm lines indicates concentration range over which the line pair selected may be used.

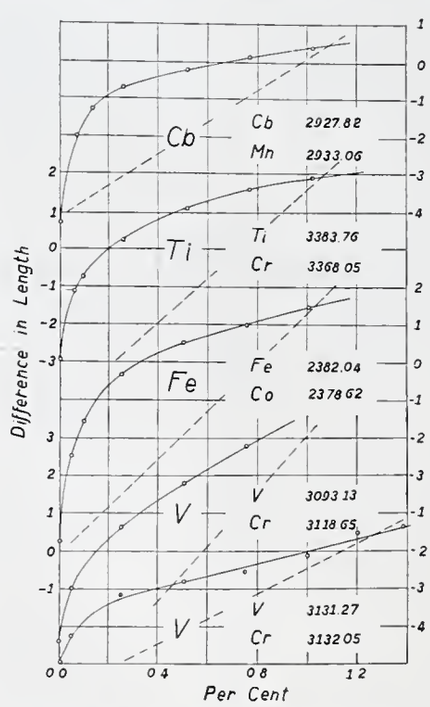

FIGURE 3. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF UNKNOWN ELEMENT FROM DIFFERENCE IN LENGTH OF UNKNOWN AND STANDARD LINES

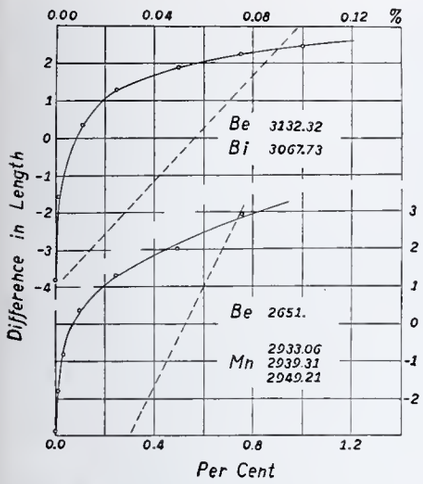

FIGURE 4. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF BERYLLIUM

0.00 to 0.12 per cent in upper curve, 0.0 to 1.0 per cent in lower curve.

ments. As will be noted, the logarithm curves have different slopes which correspond in general to the sensitivity range, chromium having a narrow range, lead a medium range, while cobalt has the widest concentration range over which this spectrographic method of analysis can be applied. This range of useful concentration for spectrographic analysis is limited on the low concentration side to the intrinsic intensity of the line and its ability to produce a reasonable photographic image, on the upper side by the point where the logarithm of the concentration plotted against the difference in line length ceases to follow the straight line obtained for the lower concentrations and begins to approach a constant value.

Within this working range of concentration the error of observation was less than 5 per cent of the observed value. While this is a rather large error where concentrations greater than 1 or 2 per cent are concerned, the value of the method increases for more dilute solutions where the error in determination of a solution containing 0.01 or 0.001 per cent of the element will still be less than 5 per cent of the observed value.

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Covering Capacity (on Water) of Aluminum Bronze Powder

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THE metallic flakes of aluminum bronze powder are characteristically different from the granular particles of nonmetallic pigments. They differ so much in shape, structure, and composition that the methods of examination and testing, well developed and standardized for other pigments, are in many cases inapplicable to the study of aluminum bronze powder. Aside from their flake-like shape and metallic base, the flakes differ from most granular pigments in having a film of polishing agent on their surface. This thin film, usually containing stearic acid as the major ingredient, modifies the appearance of the flakes and their general behavior when dispersed in a paint vehicle. The interfacial relations between powder and vehicle, as well as the size and shape of the flakes, play a part in the important phenomenon, known as "leafing."

For commercial purposes, it is customary to grade powders according to the approximate mesh size of the largest flakes. A standard varnish powder, for example, has all been through a 140-mesh screen or its equivalent. While a screen analysis may give some idea as to the major dimensions of the flakes, it tells little or nothing about their thickness (or thinness). Obviously, the thinner the flakes, the more flakes of any particular size per pound of powder. Furthermore, the thickness of flake will affect the leafing characteristics of the powder. During an investigation of the properties of aluminum bronze powder, the authors developed a method for measuring the average thickness of bronze powder flakes, which has been found very useful over a period of years. An outline of this method was first described in 1927 (*1*). Since then the method has been standardized in detail and technic of operation.

The method depends on the assumption that if all the flakes in a given weight of powder could be spread out in a film one flake thick and packed close so as to eliminate interstices between the flakes as far as possible, the thickness could be calculated from the area of the film, its weight, and the density of the powder. A film which approximates these conditions can be obtained by proper manipulation of the bronze powder on a clean surface of water. A shallow rectangular pan with a flat rim is used as the container for the water and two flat, rigid strips of glass or metal which act as barriers are laid across the width of the pan to define the ends of the film of powder whose area is to be measured. When a weighed amount of powder is carefully dusted onto the water surface which completely fills the pan, it tends to spread out in a thin leafed film. The flat barriers, resting on the rim of the pan near each end, perform a very important function in "coaxing" the powder into a film one flake thick. The results of the measurement are expressed in terms of the area in square centimeters covered by a gram of powder and this value is termed the covering capacity. It should not be confused with the so-called covering power (square feet per gallon) of a paint.

Langmuir (*2*) and others have shown how stearic acid alone can be spread out on water in a film one molecule thick, and the dimensions of the molecule estimated in this way. In this experiment the polar molecules of stearic acid are uniformly oriented with the carboxyl group directed towards the water interface. In the case of the polished aluminum flakes, the film of stearic acid, many molecules thick, appears to be oriented and fixed upon the flakes. The powder flakes in the present method are only partly wet by the water and float upon the surface. By moving the metal strips back and forth upon the side rims of the pan, the floating film of powder between them can be stretched and compressed much like a fabric until all the flakes have been brought into the water interface. The powder is then compressed by moving

one of the strips until the flakes are all touching, as determined by the tendency of the film to wrinkle with the slightest additional compression. Its area is then measured.

Detail of Method

It has been found most convenient to use a shallow rectangular aluminum pan about 14 cm. wide, 60 cm. long, and 1.3 cm. deep. The vertical walls are about 1.3 cm. thick and are machined and finished smooth on the upper surface to insure good contact with the plate glass barriers. Two pieces of heavy plate glass about 2.5 cm. wide and several centimeters longer than the width of the pan are used to confine the surface film and to work the powder uniformly over the surface of the water.

Figure 1. Test Equipment, Showing Method of Manipulation of Plate Glass Barriers

Before each determination the upper edges of the pan and the plate glass barriers should be rubbed with a piece of ordinary paraffin and the glass plates polished with a clean cloth. Water is poured into the pan until the surface is appreciably above the upper edges of the pan. The paraffined edges of the pan prevent the water from overflowing. Reasonable care should be taken to make sure that the height of the water surface above the edges of the pan is always the same. The use of distilled water is preferred and the temperature should remain constant at about 25° C.

The surface of the water in the pan is swept from end to end with one of the glass plates to remove the major portion of surface impurities, such as dust or grease. One of the glass plates is then laid across the pan near one end. Any surface impurities remaining are blown away from the water surface near the first glass barrier and the second glass plate is laid across the pan near the first, taking care that no surface impurities get between the two plates. The second barrier is then pushed nearly to the other end of the pan, sweeping all impurities before it. It is best to remove these impurities from the surface between the barrier and the edge of the pan by sweeping them over the edge of the pan with a piece of filter paper. The reason for doing this is that some of these impurities might creep under the barrier as it is moved back and forth and cause breaks in the powder film which is to be distributed on the clean water surface between the two barriers.

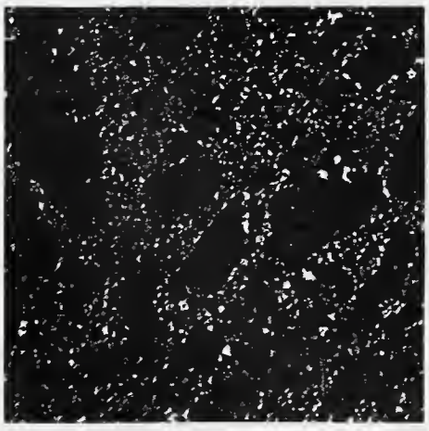

Figure 2. Photomicrograph (100 Diameters) of Compressed Film of Aluminum Bronze Powder One Flake Thick on Water

The two glass barriers are left near the ends of the pan with the clean water surface between them. An accurately weighed sample of powder is then carefully distributed upon the clean water surface. A small aluminum bottle cap makes a suitable container for weighing the aluminum powder. A piece of cheesecloth or bolting cloth may be fastened over the open end of the cap and the powder distributed on the water surface by gently tapping the inverted cap. The container should be held close to the clean water surface and moved back and forth to insure uniform distribution. An alternative method, and the one usually employed, is to pour the powder carefully from the edge of the weighing container directly onto the water surface, care being taken not to get too much powder in one place. The above operations should be carried out in a draft-free room.

After the powder has been distributed on the water surface, one of the glass barriers is pushed towards the other end of the pan, sweeping the powder before it for about two-thirds the length of the pan, and then pulled back again. This pushing and pulling operation is repeated until the powder surface is smooth and free from breaks. Leaving the first barrier in its original position, the second barrier is then moved back and forth in the same manner. The two barriers are then adjusted until there are no breaks in the metallic film and wrinkles start to form near each barrier because of too great pressure. One of the barriers is then moved back until all the wrinkles at both ends of the film are removed. This barrier is then adjusted by increasing the pressure enough to form a few wrinkles and then decreasing the pressure just enough to smooth out the wrinkles. The barrier at the other end is then adjusted slightly. The length of film between the parallel barriers is measured. The barriers are again worked back and forth three or four times, and after adjusting as before the length is measured for a second time. This procedure is repeated until the length of film remains constant for three consecutive measurements. Knowing the weight of sample and the length and width of the metallic film, the area which one gram of powder will cover can be calculated.

Figure 3. Photomicrograph (100 Diameters) of Expanded Aluminum Bronze Powder Film after Transference to Glass Slide

Figure 1 shows the test equipment and illustrates the method of manipulating one of the plate glass barriers. The film of powder is shown well worked out on the surface of the water between the barriers. The small cup used for weighing the powder and distributing it over the water appears on the table, just in front of the rectangular pan.

The weight of powder taken will depend on the size of the pan and the grade of powder used. For the pan described in this paper, a sample of standard varnish powder weighing about 0.1 gram is satisfactory. When lining powders are used, a sample weighing 0.05 gram or less will be sufficient. It is preferable that not more than about three-fourths of the cleaned water surface of the pan be covered with the powder film. Experience teaches the operator the size of sample necessary for the pan used. About 15 to 20 minutes are required for making each covering capacity measurement. A skilled operator can make duplicate measurements on the standard varnish grade of powder which will not differ in area by more than about 50 sq. cm. for 1 gram of powder. Since 1 gram of this grade of powder will cover about 4000 sq. cm. of surface, the method is reproducible to within about 1 to 2 per cent.

When pressure is applied to the uniformly distributed powder film by moving one of the glass barriers, it first wrinkles and then folds up as more and more pressure is applied. As the pressure is reduced the film unfolds to a uniform surface. This procedure can be repeated again and again without dis-

rupting the film. It appears as if only the lower side of each powder flake was wet with the water. A microscopic examination of a well-worked powder film shows that it is, for all practical purposes, only one flake thick.

In Figure 2 is shown a photomicrograph of the aluminum powder film while on the water and compressed for measurement. The photomicrograph was taken with transmitted light and any voids appear as bright spots in the picture. An approximate estimate is that less than about 3 or 4 per cent of the area appears as voids uncovered by powder.

The well-worked aluminum powder film on a water surface gives an ideal way of obtaining a slide for examination under the microscope. The pressure on the metallic film is reduced by moving one of the glass barriers towards the end of the pan. One end of a cleaned microscope slide is dipped into the water and the slide immersed for about three-fourths of its length. The slide is then carefully raised under the powder film and withdrawn from the pan. A uniform film of powder adheres to the glass slide. This film is allowed to dry on the glass slide. The size distribution of the powder particles may then be determined with the aid of a microscope.

Figure 3 shows a photomicrograph, taken by transmitted light, of a film of powder spread on a glass slide. The film is not compressed and shows the individual flakes spread out and not touching.

The covering capacity of various grades of aluminum bronze powder will range from about 3000 to 12,000 sq. cm. per gram of powder, although both higher and lower values are obtained. The low range of values is obtained with the so-called "varnish" grades of powder and the higher values are obtained with some of the lining powders. Bronze powders are usually screened during manufacture in order to limit the maximum size of particle present in any grade. Even though a screen analysis may indicate that a series of powders are very close together in mesh size, the covering test may demonstrate a considerable variation in average thickness of flake. In Table I are given data on a series of powders obtained from different commercial sources. They are graded about the same commercially, both on mesh size and appearance, but the maximum covering capacity exhibited is about 70 per cent greater than the minimum While high covering capacity is, in general, a desirable characteristic, the conclusion does not necessarily follow that the highest covering power is always the best, as other characteristics must be considered in the evaluation of a powder for any particular use.

Table I. Comparison of Covering Capacity on Water and Mesh Characteristics of Aluminum Bronze Powders

Sample	Covering Capacity	Screen Analysis: On 200-mesh screen	On 325-mesh screen	Through 325-mesh screen
	Sq. cm./gram	%	%	%
1	3040	16	30	54
2	3440	15	29	56
3	3720	12	32	56
4	4720	16	28	56
5	5260	17	28	55

While for most purposes, the covering capacity expressed in square centimeters per gram is sufficient, the calculated average thickness of flake is also of interest. The density of aluminum bronze powder is about 2.5 grams per cc. and covering capacities of 3000 to 12,000 sq. cm. per gram correspond with a flake thickness of about 0.0013 to 0.0003 mm. (0.000050 to 0.000012 inch).

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Analysis of Mixtures of Oxalic and Citric Acids by Titration with Ceric Sulfate

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The production of chemicals by the fermentative action of molds is becoming of increasing industrial importance. The present situation has been reviewed by May and Herrick (*6*). One of the most important developments is the production of citric acid, in which oxalic acid is likewise produced. In order to make adequate quantitative studies of this fermentation, a satisfactory analytical method of analysis for these acids needs to be developed, for, as stated by Currie (*2*), while the present methods "give fairly satisfactory results if used with discretion and patience, a really convenient and accurate method for estimating citric acid is still wanting." The present communication describes a method of analyzing citric acid in the presence of oxalic acid.

Oxalic acid is a very good reducing agent, and when present alone it may be titrated easily and accurately with any standard oxidizing agent such as permanganate. Citric acid, however, does not give a sharp end point with most oxidizing agents, and the final products of these reactions are not definitely known. Various methods for the analysis of citric acid have been suggested, some requiring rather elaborate manipulation. One of the most common methods, of which there are numerous modifications, is oxidation with potassium permanganate, which has been studied in different phases by Perdrix (*7*), Deniges (*3*), Pratt (*8*), Kunz (*5*), Hartmann and Hillig (*4*). Williams, Mueller, and Niederl (*10*) used a photoelectric cell in a colorimetric method, and Currie (*2*) developed a fairly accurate iodometric method.

Willard and Young (*9*) described the use of ceric sulfate as a standard oxidizing agent and applied it to the oxidation of organic matter, including oxalic and other organic acids, as did Berry (*1*). This oxidizing agent seemed to offer possibilities for the determination of oxalic and citric acids in mixtures.

Experimental

The method used is essentially differential titration of the mixture of the two acids, determining first the total acidity of the mixture by titrating with standard base using phenolphthalein and then the total reducing power of the mixture by titrating with ceric sulfate solution. While oxalic acid is oxidized quantitatively to carbon dioxide and water by ceric sulfate, citric acid is not, and the fraction oxidized is dependent upon several factors, including temperature, concentration of both sulfuric acid and ceric sulfate, and the time of standing.

Preparation of Solutions

Citric Acid. A solution of citric acid was prepared by weighing a sufficient amount of the recrystallized acid to make an approximately 0.02 N solution as an acid. This was dissolved in carbon dioxide–free water and sterilized in an autoclave under atmospheric pressure for 30 minutes. To this solution, after cooling, were added 2 drops of chloroform to prevent the growth of molds. After titration with standard base, this solution was diluted to make it exactly 0.02 N.

Figure 1. Titration of 0.01 N, 0.02 N, and 0.05 N Acid Mixtures

Oxalic Acid. A solution of 0.02 N oxalic acid was prepared in a similar manner, except that the sterilization was omitted. Another oxalic acid solution to be used for back-titration was prepared and standardized against the ceric sulfate solution.

Ceric Sulfate. A ceric sulfate solution, prepared from pure ceric oxide according to the method of Willard and Young (*9*), did not give a sharp break when titrated electrometrically against sodium oxalate. When the technical oxide was used instead of the pure oxide, the break obtained was sharp. Formation of colloidal material in dissolving the oxide caused some difficulty, but this was overcome by changing the method of preparation. The method used is as follows:

Six hundred cubic centimeters of concentrated sulfuric acid in a 12-liter balloon flask were placed in a sand bath on an electric hot plate. A sturdy glass stirrer, run by a 0.125-horsepower motor, was introduced through a three-holed stopper. Through a second hole the ceric oxide was added, the third hole serving as a vent. Six hundred grams of ceric oxide were added, with constant stirring, while the solution was kept at 135° to 140° C. and the reaction allowed to continue for 4 hours, during which time the mixture became a paste. Sufficient water was added from time to time to maintain it as a paste. After 4 hours it was slowly diluted to 8 liters with water and heated at almost a boiling temperature for 8 hours. After settling, the clear reddish amber liquid was siphoned off and filtered while hot. The clear liquid was heated to about 90° C., and after adding 150 cc. of concentrated sulfuric acid was held at that temperature for from 24 to 30 hours. After filtering through a Gooch crucible, it was standardized against sodium oxalate. The solution should be between 0.1 N and 0.14 N if made in this manner. The ceric sulfate was standardized against pure sodium oxalate by dissolving 0.2 gram of the latter in 20 cc. of water and adding 2 cc. of 1 to 1 sulfuric acid. This was heated to 80° C. on an electric hot plate and titrated electrometrically with the ceric sulfate. An excess of 0.2 cc. of the latter will turn the solution a light yellow color and the potential change at the end point for 0.1 cc. of ceric sulfate is 0.2 volt. The end point is very sharp and definite.

Analysis

For the oxidation of citric acid 25 cc. of the 0.02 N solution were treated with 75 cc. of the ceric sulfate solution to which 2 cc. of 1 to 1 sulfuric acid had been added. This mixture was heated in a water bath, the vessel containing the sample being immersed in the water at 90° to 95° C. for 1 hour. The excess of the ceric sulfate was determined by titrating with standard oxalic acid electrometrically, heating the solution on a hot plate during the titration. The end point is obvious because of the decolorization of the ceric sulfate as it is reduced. Twenty-five cubic centimeters of the citric acid (0.02 N as an acid) required 22.91 cc. of the 0.1148 N ceric sulfate. Assuming that the citric acid is oxidized completely to carbon dioxide and water according to the equation

$$2C_6H_8O_7 + 9O_2 = 12CO_2 + 8H_2O$$

the tribasic acid is equivalent to 18 valence changes, as a reducing agent, and should therefore have a normality six times as great as a reducing agent than as an acid. The percentage oxidation in the above titration is given by the expression

$$\frac{(22.91)(0.1148)}{(25)\ (0.02)\ (6)} = 0.877 = 87.7 \text{ per cent}$$

Oxalic acid is oxidized quantitatively to carbon dioxide and water.

Three series of mixtures of oxalic and citric acids were prepared and oxidized in a similar manner. In Table I are given the cubic centimeters of 0.1074 N ceric sulfate required to oxidize 25 cc. of these acid mixtures, which were 0.02 N, 0.01 N, and 0.05 N, respectively, as an acid.

Table I. Titration of Acid Mixtures

0.01 N Acid			0.02 N Acid			0.05 N Acid		
Oxalic acid	Citric acid	0.1074 N ceric sulfate	Oxalic acid	Citric acid	0.1074 N ceric sulfate	Oxalic acid	Citric acid	0.1074 N ceric sulfate
%	%	Cc.	%	%	Cc.	%	%	Cc.
100	0	2.38	100	0	4.67	100	0	11.76
92	8	2.78	96	4	5.10	96	4	13.36
84	16	3.54	92	8	5.74	92	8	15.51
72	28	4.72	84	16	7.35	88	12	17.60
20	80	10.13	80	20	8.17	80	20	21.36
0	100	12.18	50	50	14.23	...	..	...
...	...	...	20	80	20.31	...	..	...
...	...	...	0	100	24.40	...	..	...

The data from Table I were plotted in Figure 1. With the exception of the points for the high percentages of oxalic acid the curves are straight lines. In the 0.05 N solutions, the higher concentrations of citric acid do not give a sharp

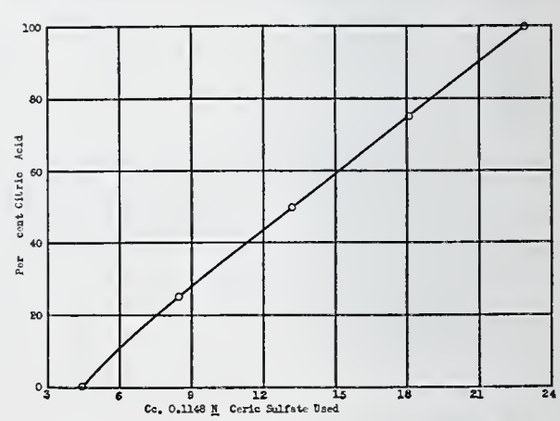

Figure 2. Determination of Acids after Precipitation

end point. With the 0.01 N and 0.02 N solutions it is possible to use only 50 instead of 75 cc. of the ceric sulfate solutions and still get complete oxidation, but if this is done it is better to use but 1 cc. of the 1 to 1 sulfuric acid instead of 2.

A series of mixtures of the two acids was made by weighing out varying amounts of each, dissolving, and titrating the total acidity with standard sodium hydroxide. Portions of these which were equivalent to 25 cc. of 0.02 N acid were titrated with cerium sulfate solution. The data obtained are given in Table II, together with the percentages of the two acids as calculated from the titration curve.

Table II. Percentages of Acids from 0.02 N Curve

By Weight Oxalic	By Weight Citric	0.1074 N $Ce(SO_4)_2$ Used	By Titration Oxalic	By Titration Citric
%	%	Cc.	%	%
91.64	8.36	5.77	91.9	8.1
78.58	21.42	8.24	79.8	20.2
67.00	33.00	10.30	69.5	30.5
61.41	38.59	11.65	62.8	37.2
39.01	60.99	16.38	39.6	60.4
22.07	77.93	19.96	22.2	77.8

Another series was made by weighing different amounts, titrating with standard base, diluting aliquot portions to both 0.02 N and 0.01 N, and then titrating 25 cc. of each with ceric sulfate. From the titration values the percentages of the two acids present were calculated, using the curves. The data are given in Table III.

Table III. Percentage of Oxalic and Citric Acids

By Weight Oxalic	By Weight Citric	0.1074 N Ceric Sulfate	From Curve Oxalic	From Curve Citric
%	%	Cc.	%	%
		from 0.02 N curve		
85.77	14.23	7.03	85.8	14.2
69.08	30.92	10.42	69.0	31.0
53.34	46.66	13.60	53.5	46.5
38.28	61.72	16.71	38.1	61.9
21.48	78.52	19.98	21.8	78.2
		from 0.01 N curve		
85.77	14.23	3.33	86.0	14.0
69.08	30.92	5.00	69.4	30.6
53.34	46.66	6.58	54.2	45.8
38.28	61.72	8.15	39.0	61.0
21.48	78.52	9.87	22.2	77.8

Separation from Other Organic Acids

Since in the process of fermentation these acids are produced along with other acids, it is necessary to separate them from the mixture before analyzing by the above method.

The first attempt to bring about this separation was by precipitating them as the barium salts, washing the precipitate until free from acid, and then adding an excess of sulfuric acid which precipitated the barium and changed the oxalic and citric acids back into the free acids. The excess of sulfuric acid was then removed by adding an excess of benzidine. This process should leave the free oxalic and citric acids with the excess of benzidine and it was hoped that they could be titrated in this mixture. Two difficulties were encountered—the benzidine was oxidized by the ceric sulfate and the precipitation of the excess of sulfuric acid in this solution by benzidine was not quantitative—and the method was therefore abandoned.

The second method was to precipitate the two acids as the lead salts, filter and wash free from acid, suspend the precipitate in water, and pass in hydrogen sulfide to precipitate the lead. The excess of hydrogen sulfide was removed from the solution by passing nitrogen gas through the solution until no test was given with lead acetate paper. This solution was then titrated with standard base, diluted to 0.02 N as an acid, and titrated with the ceric sulfate solution.

Three solutions of different normalities, all containing 42.6 per cent of oxalic acid and 57.4 per cent of citric acid, were prepared and treated as above. The separated acids were titrated with standard base, and amounts equivalent to 25 cc. of 0.02 N acid were titrated with the ceric sulfate solution. Seventy-five cubic centimeters of 0.1148 N ceric sulfate solution were added and the excess titrated with oxalic acid, 1 cc. of which was equal to 2.556 cc. of the ceric sulfate solution. The results are given in Table IV, in which the percentages of the two acids are obtained from Figure 2, which shows the relationship between the amounts of 0.1148 N ceric sulfate solution used in titrating 25 cc. of 0.02 N acid mixture and the percentages of the acids present. For accurate work this curve should be drawn on a large scale to enable one to read small amounts.

Table IV. Determination of Acids after Precipitation

Normality of Acids	Sample Used	Oxalic Acid Used	0.1148 N $Ce(SO_4)_2$ Used	Oxalic Acid	Citric Acid
	Cc.	Cc.	Cc.	%	%
0.02318	21.57	23.71	14.40	43.2	56.8
0.02571	19.45	23.70	14.42	43.0	57.0
0.02457	20.35	23.63	14.60	42.2	57.8

This shows that the percentages of the two acids present in a given mixture may be determined with an error of less than 1 per cent of the amounts present. Considering that the solutions used are but 0.02 N, the total acid present in 25 cc. would be but (0.02) (25) (0.045) gram of oxalic acid = 0.0225 and 1 per cent of this or 0.000225 gram is the error in weight due to the method.

Conclusions

A method has been developed for the analysis of mixtures of citric and oxalic acid by a differential titration, first as an acid and then by oxidation with ceric sulfate.

The accuracy is about 1 per cent of the total acid present.

The two acids may be separated from mixtures of other organic acids obtained in fermentation processes by the insolubility of their lead salts. These salts are changed back to the free acids by treatment of the suspension of the lead salts with hydrogen sulfide, and after filtering the excess of hydrogen sulfide can be removed by passing nitrogen gas through the solution.

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Italian Sponge-Processed Lemon Oil Situation. The February drop in quotations for Italian sponge-processed lemon oil to 4.50 lire per Sicilian pound, from the previous month's ruling quotation of 6.00 lire, was considered particularly serious, in view of the relatively high cost of the fruit. It is estimated locally that 1000 lemons yield 1.5 Sicilian pounds of oil and 3 kg. of citrate of lime, the total value of which at February quotations was not over 12.75 lire. The fruit itself cost about 8 lire per thousand. When other expenses were added, the prices mentioned above resulted in a definite loss. Producers are agitating vigorously for some action on the part of the government. Lack of demand and lack of ready cash resulted in sales at any prices offered. In spite of the striking drop in prices, foreign demand was weak, whereas in preceding months, with much higher prices prevailing, there was much greater activity. Local well-informed sources rejected the supposition that foreign oil stocks were of sufficient size to account for the lull, and contended that, for some years past, no stocks of lemon oil had been created abroad. It is said that the price drop was probably due to a combination of factors, which included: the deliberate abstention from purchasing, by local exporters, with a view to further depressing the price level; the large stocks remaining from last year (which are said, inclusive of machine production, to have exceeded 1,600,000 Sicilian pounds), and the tightness of money.

Choice of Catalysts for the Hydrogen Electrode

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IN SPITE of the universal use of the hydrogen electrode, the metals available for the purpose have not been very systematically investigated. In a recent paper (*2*) there appeared a study of such catalysts which the writer wishes to supplement here, especially with the view of furnishing a practical guide to the laboratory technician.

Considerations Governing Choice of Catalysts

Hydrogen-electrode catalysts gradually lose their activity when exposed to hydrogen. This decay is produced by the hydrogen itself, although of course certain impurities when present may cause a so-called poisoning of the catalyst distinct from the above effect. In some cases the poisoning by impurities is more pronounced than the deactivation by hydrogen; in others the reverse is the case. Catalysts retain their activity when stored in oxygen or air.

Freshly electroplated platinum or iridium is always highly active, whether the deposit is smooth or black. The rate at which these deposits become deactivated when in use depends on their thickness and on the rate at which they are plated. Thick deposits, especially if plated very slowly, remain active for a longer time.

The decay of hydrogen-electrode catalysts is enormously accelerated by an increase in the temperature. Because of this a dry electrode may become entirely inactive when taken from the air into a hydrogen atmosphere, owing to the combination of the two gases at the surface, even if for only a fraction of a second. Previous wetting of the electrode is a necessary precaution when making a transfer of this kind.

Deviations from the equilibrium hydrogen potential are due to polarization of the hydrogen electrode by substances capable of oxidizing activated hydrogen or reducing hydrogen ion; and to leakage of H^+ (adsorbed during plating) from the electrode and consequent change in the H^+ concentration at the electrode surface. Polarizing impurities are found both in the solution (traces of dissolved oxygen) and in the electrode itself (base metals dissolved in the platinum). The effect of these impurities on the potential depends on their concentration and on the catalytic activity of the electrode, being less the greater the catalytic activity. Poisons do not directly cause deviations from the equilibrium potential but indirectly by affecting the catalytic activity. Because commercial gold (foil or wire) is usually much purer than commercial platinum, it makes a very desirable base for plating the catalysts.

The following recommendations are made as to the choice of catalysts:

For decidedly acid or basic solutions or for strongly buffered neutral solutions and also for maximum resistance to the action of poisons, platinum black.

For unbuffered neutral or slightly acid solutions, bright thin deposits of platinum or iridium. It may be desirable to plate these deposits from an alkaline bath in order to minimize the adsorption of H^+ by the metal (*1*).

For slightly basic, unbuffered solutions, bright thin iridium.

Preparation of Catalysts

The quality of the deposits is impaired by evolution of hydrogen or by the uneven plating resulting when too great a portion of the current merely reduces the ions to a lower valence without forming metal. For these reasons the concentration of the plating bath is specified and stirring is recommended in some cases, and not in others. The current densities should be as small as possible. The finished electrodes may be stored in distilled water with access to air. They should never be treated with chromic acid.

Platinum Black. This is plated with slow stirring from a 2 per cent solution of chloroplatinic acid containing a trace of lead acetate, which seems to promote adhesion of the deposit to the base. The current should be about 60 milliamperes per sq. cm. for 1 to 2 minutes. Nothing is gained by making the deposit very thick or by reversing the current at intervals. It is advisable to allow the electrode to stand a few hours in distilled water before using it.

Bright Platinum. The plating solution is prepared by heating chloroplatinic acid on a sand bath to about 300° C. for an hour. The residue is dissolved in hydrochloric acid to give a 2 per cent solution of chloroplatinous acid in 1 *M* hydrochloric acid. The current density in this bath should be about 1 milliampere per sq. cm. or less for 10 to 30 minutes without stirring.

If an alkaline plating bath is to be used, a 0.5 per cent solution of sodium chloroplatinate plus sodium hydroxide is prepared. The current density in this case will have to be high (10 milliamperes per sq. cm. or more) and no stirring used. The plating is continued until the thickness is 2 to 6 times that necessary just to cover the base. Beyond this thickness, increase in the objectionable features of the deposit (loss of smoothness) offsets any gain in the desirable ones (increased resistance to decay).

Bright Iridium. The material for the plating bath is obtainable on the market in a form usually labeled iridium tetrachloride. A dilute solution of this (about 0.1 to 0.5 per cent) is used as a bath. The best results are obtained by using between 0.1 and 1.0 milliampere per sq. cm. and allowing enough time to give a total thickness of from 2 to 6 times that which will just cover the gold base. This may require 3 or 4 hours. The bath should not be stirred.

Table I. Catalytic Activity and Decay of Electrodes

(In 0.1 *N* hydrochloric acid)

Time of Exposure to Hydrogen	Bright Palladium	Bright Platinum	Bright Iridium
Hours	*Amperes/ volt/sq. cm.*	*Amperes/ volt/sq. cm.*	*Amperes/ volt/sq. cm.*
5	0.000035	0.019	0.020
23	0.0000041	0.017	0.019
48	0.0000035	0.013	0.016

Palladium Electrodes

Many investigators have used palladium electrodes in the belief that a high capacity for hydrogen absorption necessarily implies good hydrogen-electrode properties. There is, however, very little connection between the absorption capacity and the catalytic activity of the surface for hydrogen activation, which latter is the quality desired in a hydrogen electrode. Palladium is not very active in this respect when compared to platinum or iridium and, even though palladium black may be sufficiently active to serve (because of sheer extent of area), still it is so far short of platinum black that there can be no advantage in its use. A comparison of the catalytic activity of bright palladium with that of bright platinum and bright iridium brings out the tremendous difference very clearly. A typical test is shown in Table I. The measure of catalytic activity is the slope of the polarization curve at the equilibrium potential (*2*).

Checking Validity of Hydrogen-Electrode Potentials

It is common practice, when determining hydrogen-ion activity, to use two or more electrodes together. It is considered that the agreement of several electrodes is a satisfactory indication that they have reached the desired potential. With identical preparation of the catalysts we may expect them to have similar properties and that the effect of polarizing impurities on all electrodes may be the same—that the potentials will show close agreement even though they be far from the equilibrium value. The only certainty that we are reading the true equilibrium potential is by the agreement of electrodes of widely different catalytic activities. The preparation of electrodes of low activity is best accomplished by allowing bright electrodes to age in hydrogen a few days. They should not, however, be allowed to become too inactive, as an activity less than 0.001 makes the catalyst impractical for the purpose. For most ordinary work such refinement is not necessary.

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Received December 30, 1933. In part based upon a dissertation submitted by Arthur E. Lorch to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of doctor of philosophy, May 16, 1932.

A Method for Measuring the Dew Point of Natural Gases[1]

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A GREAT quantity of natural gas escapes from the wells in oil fields. The greater part of this gas is methane, and the remainder is mostly a mixture of saturated hydrocarbons up to hexane, of which the higher-boiling constituents are valuable for addition to the low-boiling fractions of the natural oil. The separation of the higher homologs in the gas is usually carried out by compressing to about 20 atmospheres at most, and cooling to about −10° C. The object of the work described here was a study of the dew point of a gas mixture with a view to establishing the most efficient conditions for the extraction of the higher homologs.

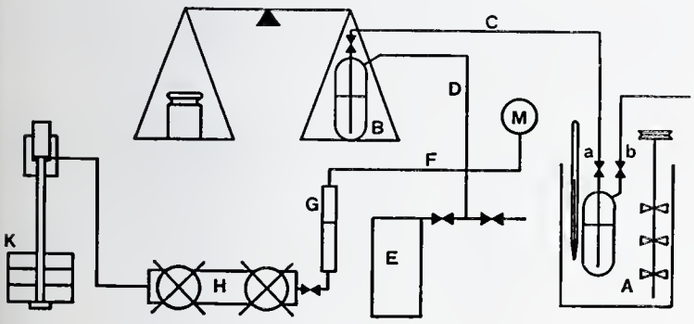

Figure 1. Diagram of Apparatus

The Method

When an ideal gas (Boyle gas) is compressed at constant temperature, the product, pv, is independent of the pressure. In the case of a real gas, however, the value of pv changes with pressure, so that if pv is plotted against p, a curve is obtained which runs smoothly up to the pressure at which condensation of the gas starts. At this point there is a break and the curve becomes a straight line perpendicular to the p axis, as it is impossible to increase the pressure at constant temperature until all the gas has been liquefied. With a mixture of gases there is also a break in the curve at the condensation point, but the value of p does not remain constant during condensation and therefore the pv-p curve does not become perpendicular to the p axis. The difference in the slope of the two parts of the curve on each side of the break depends on the composition of the gas and also on the temperature. The higher the temperature the smaller the change in slope, until it becomes zero at the critical point of the mixture. It follows that the dew pressure can be determined by measuring the isotherm.

The Apparatus

The use of an ordinary Cailletet piezometer, in which the gas is compressed into a narrow glass capillary tube, would obviously be unsatisfactory, because, as soon as liquid is formed, small drops might stick to the wall of the capillary tube and be enclosed by the mercury when this rises.

A diagrammatic sketch of the apparatus used by the authors is given in Figure 1.

Two high-pressure gas cylinders, A and B (volume about 600 cc.), are connected with the steel capillary C, which reaches the bottom of the gas cylinders. Both cylinders, when in use, are partly filled with mercury. The gas under investigation fills the upper half of cylinder A. The top of B can be filled with nitrogen from cylinder E. Cylinder A is placed in a thermostat, the temperature of which can be regulated to within 0.01° while

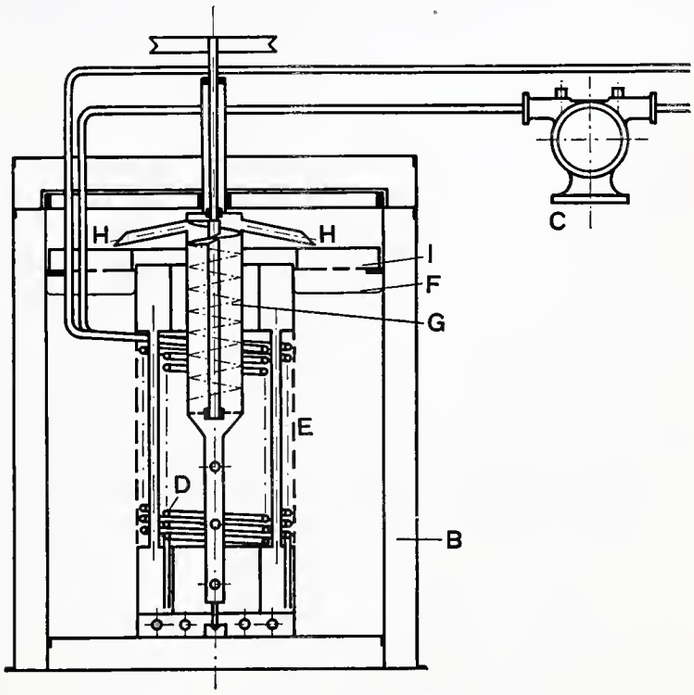

Figure 2. Diagram of Thermostat

[1] Thirty-fourth publication of the v. d. Waals fund, Amsterdam, Holland.

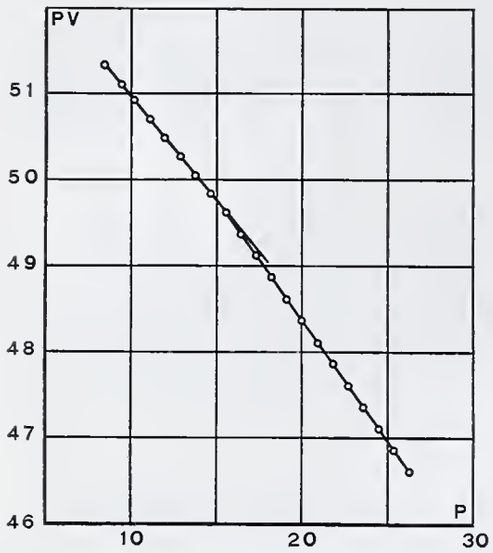

Figure 3. Isotherm at 0° C.

cylinder B stands on one scale pan of a balance. The steel capillaries D and C (1.2 mm. outer, 0.8 mm. inner diameter) are flexible enough to give a balance sensitivity of 4 scale divisions per gram. To compress the gas under investigation the tap leading from cylinder E is opened, and the pressure of nitrogen in cylinder B increases, forcing the mercury through capillary C into bomb A. The decrease in volume of the gas in A is equal to the volume of the mercury displaced from B, which can be calculated from the loss in weight of B. For accurate measurements of the pressure a pressure balance was used. Tube F leads to a leveling gage, G, which is coupled to the press, H, and from here to the pressure balance, K. When pressure equilibrium is reached, the pressure of the gas in A can be calculated from the load on the pressure balance, corrections being applied for the hydrostatic pressures of oil between K and the oil level in G, of nitrogen between G and the mercury level in B, and of the mercury between the levels in A and B.

Temperature Control

The bomb which contains the gas to be examined is placed in a well-insulated thermostat. Above room temperature heating control as described by one of the authors (*1*) is used. Between room temperature and 0° the thermostat is cooled with the help of a cooling coil and the temperature is regulated in the same way. As it is essential for good regulation of temperature that the amount of heat removed from the thermostat by the cooling coil shall not fluctuate too rapidly, an arrangement was made whereby cooling liquid of constant temperature was introduced at constant rate into the cooling coil (Figure 2). Kerosene was used as the cooling liquid, being precooled in another copper coil, D, placed in a second double-walled vessel, B. The kerosene was circulated by a piston pump, C, running at constant speed.

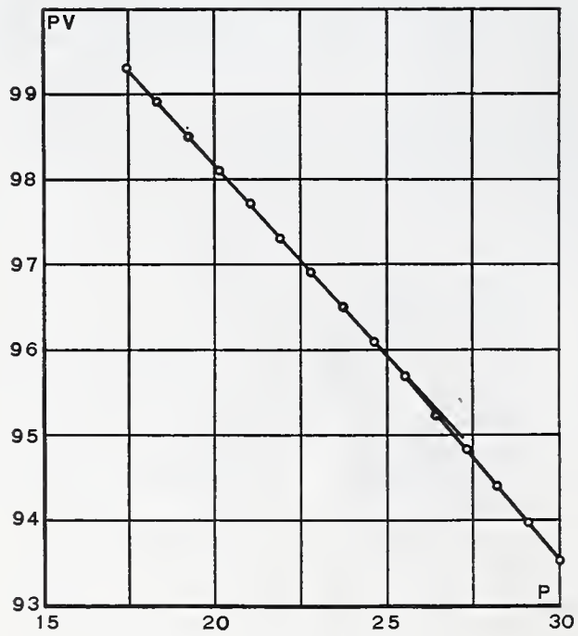

Figure 4. Isotherm at 10° C.

In practice it is preferable not to place coil D directly in ice, but to cool it with water of nearly 0° C. The arrangement used is shown in Figure 2. Spiral D was surrounded by the tinned copper gauze, E, and the space between E and the wall of the vessel filled with chopped ice. The vessel was then further filled with water, until level F was reached. An Archimedes screw pump, G, sucked the water past the windings of the coil and poured it out again at H into tray I, the bottom of which is riddled with small holes, thus giving a reasonable distribution of the water over the top of the ice.

Measurements and Results

Measurements were carried out on natural gas, obtained from the Dutch East Indies. The gas had been passed through a commercial condensation apparatus and was stored in a steel bomb of 50-liter capacity. The measuring apparatus was to be filled directly from this bomb and as some of the higher homologs might have condensed in the bomb,

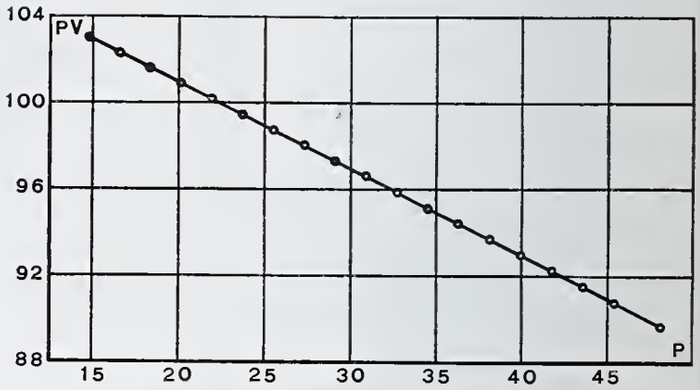

Figure 5. Isotherm at 21° C.

it was heated up to 40° C. just before filling. The analysis of the gas, as carried out with a Podbielniak rectifying apparatus, was as follows:

	Mole Per Cent
CO_2	0.6
O_2	0.3
N_2	1.2
CH_4	74.9
C_2H_6	12.0
C_3H_8	6.7
C_4H_{10} (iso)	1.9
C_4H_{10} (n)	1.3
C_5H_{12} (iso)	0.8
C_5H_{12} (n)	0.1
C_6H_{14}	0.2

Measurements were carried out at temperatures of 0°, 10°, and 21° C. The results are shown in Figures 3, 4, and 5 in which the values of pv are plotted against p. The values of pv were obtained by multiplying the pressure in atmospheres by the volume of the gas in an arbitrary unit. By this method the normal volume of the gas—i. e., the volume at 1 atmosphere and 0°—was not measured; therefore it was not possible to express the figures in standard units. From the figures it can be seen that at 0° the gas starts to condense at a pressure of 15.5 atmospheres and at 10° C. at 25.5 atmospheres, whereas there is no obvious break in the 21° C. curve. Therefore the critical temperature of the mixture is probably below 21° C.

Acknowledgment

The authors wish to thank the Bataafsche Petroleum Company, and especially the Research Department for their collaboration which enabled this work to be undertaken.

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A Photronic Colorimeter and Its Application to the Determination of Fluoride

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In connection with the study of natural waters, a need was felt for a photoelectric colorimeter, and after some preliminary experimental work the apparatus here described was assembled. It uses as its light-measuring elements two Weston photronic cells, which are photoelectric cells of the type that transforms light energy directly into electrical energy without the use of an external e. m. f. In the present assembly the cells are electrically opposed and the current developed by them is balanced by means of a variable resistance. A sensitive galvanometer is used as the indicating instrument. The intensity of the light transmitted through a colored solution is measured in terms of the resistance that must be interposed to balance the photronic cells.

The apparatus has been satisfactorily used for the determination of fluoride in natural waters by a modification of the acetylacetone method described by Armstrong (*1*). In earlier tests the thiocyanate reagent and method, essentially as described by Foster (*3*), were used, but it has been found that the acetylacetone reagent is somewhat less susceptible to the effect of sulfate and chloride than the thiocyanate reagent.

Description of Apparatus

A schematic diagram of the apparatus and circuit is shown in Figure 1.

The light, *W*, is a 50-watt, 110-volt mill-type bulb. The plate-brass light housing has a ground-glass covered opening, *D*, 0.5 inch (1.27 cm.) in diameter in each light path. Heavy, seamless brass tubes 2.06 inches (5.2 cm.) inside diameter connect the light openings with the solution cabinets, or boxes, B_1 and B_2, and like tubes, in turn, connect these with the photronic cells, *P*, *P*, mounted in the two extremities. The lenses, *L*, between the light and the boxes, render the light rays parallel and those beyond the boxes converge them slightly toward the faces of the photronic cells. Slit S_1 has two moving parts and can be adjusted from a fully open position to completely closed. Slit S_2 has a single moving part which, when closed, will cover about one-third of the light path.

The Model 594 Weston photronic cells are of photovoltaic type and in operation resemble ordinary voltaic cells. The positive poles are connected directly and the negative poles are connected through the resistances. The variable resistance is a decade box of 11,110 ohms in steps of 1 ohm. The fixed resistance has a value of 1000 ohms. The galvanometer has a sensitivity of 0.025 microamperes per scale division. The resistance of the coil of the galvanometer is 1000 ohms. The 110-volt alternating current circuit, not shown, includes a switch and a double outlet for the lamps of the colorimeter and the galvanometer.

It was originally planned to compare the reference and unknown solutions. For this purpose two boxes, B_1 and B_2 of Figure 1, were provided in the set. To make such a measurement, the set is balanced, as indicated below, with a cell filled with the reference solution in each box. The reference solution in the cell in box B_2 is replaced by the unknown solution and the set is balanced by adjusting the variable resistance, *VR*. The change in this resistance from the original setting of 1000 ohms to some new value measures the difference in light transmission of the two solutions. For the present purpose this offers no advantage, but there may be applications where it would be desirable. Likewise, the use of all-glass cells arranged in a horizontal position or Nessler cylinders in a vertical position might be indicated. Such modifications could be made without changing the electrical circuit.

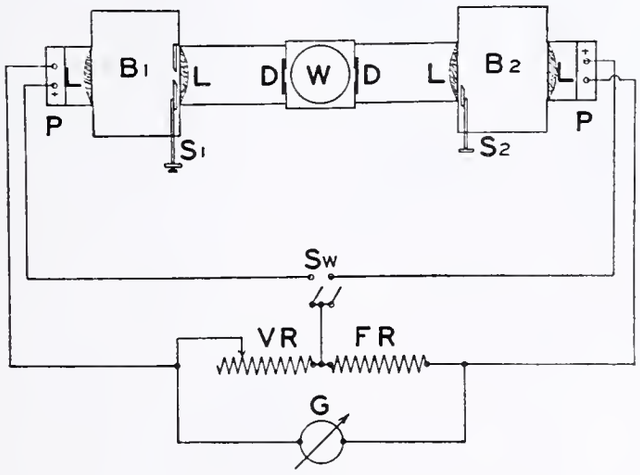

Figure 1. Diagram of Photronic Colorimeter, Showing Electrical Circuit

VR. Variable resistance
FR. Fixed resistance
G. Galvanometer
Sw. Double-pole single-throw switch
S_1, S_2. Variable slits
P. Photronic cells
L. Lenses
B_1, B_2. Boxes
D. Ground glass over openings
W. Light

The general arrangement of the set is shown in Figure 2. In the foreground are two glass cells of the type used. They are of metal, lacquered inside, with plain glass sides. To the left of the cells is an amber-colored glass, the resistance reading of which is frequently noted as a measure of the reproducibility of the instrument. The resistance required to compensate for this glass is 390 ohms, with variation from day to day not exceeding ±3 ohms.

Operation of Photronic Colorimeter

Fifteen minutes before use, the lamps of the set and the galvanometer are turned on. The variable resistance, *VR*, of Figure 1, is set at 1000 ohms and the switch, *Sw*, is left open. Ten minutes later, the switch is closed and the slit, S_1, is adjusted until the galvanometer shows no deflection. The set is then kept in balance by adjusting the slit until it remains in equilibrium. This requires only a few minutes, after which the set is ready for use. The switch is opened and into the box, B_2, a reference solution in a glass cell is introduced. The switch is closed and the set brought back to balance by means of the variable resistance. (The adjustment of the slits should not be disturbed during the measurements.) The resistance is recorded.

The process is repeated with the unknown solution substituted for the reference solution, using the same glass cell.

The ratio of the resistance reading of the unknown solution to that of the reference solution bears a definite relationship to the concentration of the unknown solution. The method of establishing and interpreting this relationship will be discussed below.

Glass light-filters may be substituted in place of the ground-glass disks, *D*, Figure 1. For the fluoride determination green glass filters, having a low transmission in the red, increased the sensitivity appreciably.

Where small differences are significant, scrupulous cleanliness of the optical parts and the cells must be maintained. The condition of the apparatus in this respect can best be determined by measuring frequently the resistance of the cell filled with distilled water.

The switch, *Sw*, Figure 1, should not be closed for any length of time when the set is far off balance as a condition ensues which, in effect, resem-

bles polarization and from which the photronic cells recover rather slowly.

The electrical circuit here presented offers several advantages: a balanced circuit, which largely eliminates effects resembling polarization; a "null" measurement, indicated by a sensitive galvanometer; recorded values in terms of ohms resistance rather than scale divisions; quickly established equilibrium; and a negligible drift.

Determination of Fluoride in Natural Waters

The procedure described by Armstrong (*1*) has been adapted for use with the photronic colorimeter. Only minor changes were found necessary.

Reagents. Ferric nitrate solution, 1 cc. = 0.2 mg. of iron in 0.02 *N* nitric acid; acetylacetone solution, 0.35 per cent aqueous solution; standard fluoride solution, 1 cc. = 0.1 mg. of fluoride; salt solution, 29.2 grams of sodium chloride and 30.1 grams of magnesium sulfate in 1000 cc. of water; 0.1 *N* nitric acid; *p*-nitrophenol indicator solution, 1 gram in 100 cc. of 70 per cent ethyl alcohol; approximately 1.0 *N* nitric acid; sodium hydroxide, carbon dioxide–free, approximately 0.5 *N*.

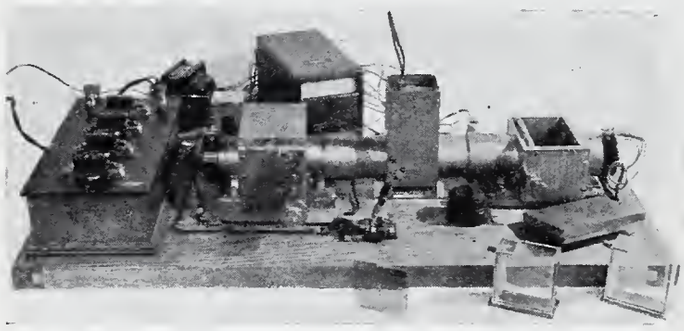

Figure 2. Photograph of Photronic Colorimeter

Procedure. Transfer an aliquot of 100 cc. of the water or an aliquot containing not more than 0.5 mg. of fluoride to a 250-cc. beaker. Add one drop of *p*-nitrophenol indicator and 1.0 *N* nitric acid until colorless and 0.5 cc. excess. Bring to a boil and allow to boil 2 minutes, stirring vigorously to expel carbon dioxide. Remove from the flame and cool to room temperature.

While the samples are cooling, prepare the ferric-acetylacetone reagent, 10 cc. for each determination, as follows: 3 parts of acetylacetone solution, 2 parts of salt solution, 5 parts of ferric nitrate solution. Mix and allow to stand until ready for use.

When the samples are cool, add carbon dioxide–free 0.5 *N* sodium hydroxide until a faint yellow color of *p*-nitrophenol develops. Adjust to colorless with 0.1 *N* nitric acid, adding one drop in excess.

Make up to 110 cc. Add 10 cc. of the ferric-acetylacetone reagent and mix. After 10 minutes, compare in the photronic colorimeter as described above. With each set of determinations, include a sample of distilled water containing all the reagents but no fluoride. Calculate the ratio of the resistance reading of the unknown to that of the fluoride-free sample and read the fluoride concentration of the unknown from curves worked out in the calibration of the instrument.

Solutions of known fluoride concentration covering the range from 0 to 5 p. p. m. were made up with distilled water and analyzed by the procedure described above. The results are shown in Table I.

Table I. Analysis of Pure Fluoride Solutions

Fluoride	Variable Resistance Reading: Fluoride solution	Variable Resistance Reading: Blank[a]	Ratio[b]
P. p. m.	*Ohms*	*Ohms*	
0	523	523	1.000
0.5	534	523	1.021
1.0	549	523	1.050
2.0	570	523	1.090
3.0	591	523	1.130
4.0	612	523	1.170
5.0	633	523	1.210

[a] Resistance required to balance a solution of the reagents in distilled water, in this case, the 0 p. p. m. fluoride solution.
[b] Obtained by dividing the figures of column 2 by the corresponding figures in column 3.

It will be seen from these figures that for a change of 5 p. p. m. of fluoride the resistance changed 110 ohms or an average of 22 ohms per p. p. m. Thus the indicated sensitivity for a change of one ohm is 0.05 p. p. m. of fluorine. The accuracy of the method is discussed below.

Table II. Effect of Sulfate and Chloride on Determination of Fluoride

Anion	Concentration *M.E./liter*[a]	Ratios of Resistance in Salt Solutions to Resistance in Distilled Water: Fluoride, 0 p. p. m.	Fluoride, 5 p. p. m.
Sulfate	0	1.000	1.210
Sulfate	10	1.019	1.210
Sulfate	20	1.025	1.216
Chloride	0	1.000	1.210
Chloride	20	1.000	1.207

[a] Milligram equivalents per liter.

The effect of chloride has been investigated over a greater range than is reported in Table II, and it is believed that the effect of this ion may be neglected in concentrations not exceeding 25 milligram equivalents per liter. Silica, borate, and phosphate, in amounts normally present in natural waters, likewise appear to be without measurable effect. Hydrogen ion is controlled sufficiently accurately by the procedure indicated above but it should be emphasized, in this connection, that carbonates must be expelled.

Sulfate appears to be the only ion commonly found in natural waters for which a correction must be made in the colorimeter readings.

The reagents here differ somewhat from those suggested by Armstrong. The salt solution is an addition to the list. In its absence, the bleaching effect of chloride and sulfate is much greater. Ferric nitrate in nitric acid is much more stable than ferric chloride. Such solutions have been in use for several months and appear to be unchanged.

Calibration

Solutions of known fluoride concentration covering the range from 0 to 5 p. p. m. are made up with distilled water and analyzed by following the procedure described above. On one axis the fluoride concentration in parts per million is plotted and of the other the ratio of the resistances of the fluoride solutions to that of the fluoride-free solution. Such a curve is shown in Figure 3.

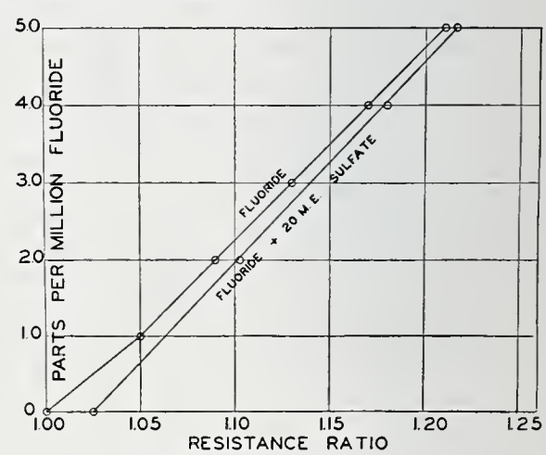

Figure 3. Resistance Ratios at Various Fluoride Concentrations in Presence of Sulfate

The only ion thus far encountered in the natural waters of the West that measurably interferes with the fluoride determination is sulfate. It appears to be very difficult, if not impossible, to remove this constituent without a loss of fluoride, but, in view of the fact that the effect is approximately linear and additive, the correction for it is comparatively simple.

Prepare a set of pure fluoride solutions, as directed above, to which add 20 milligram equivalents of sulfate per liter, assuming

a 100-cc. sample. Complete the determinations and plot the curve. It will be found to be below but nearly parallel to the first, as reference to Figure 3 will show. In like manner complete additional curves to cover the range of sulfate likely to be encountered. Then, knowing the sulfate concentration of the sample, the fluoride concentration can be determined by interpolation. For example, suppose the determined resistance ratio is 1.150. If sulfate is absent, the indicated fluoride concentration is 3.5 p. p. m. If there are 10 milligram equivalents of sulfate, the corresponding fluoride is 3.4 p. p. m., and for 20 milligram equivalents the fluoride is 3.25 p. p. m.

Analytical Results

Fluoride determinations on a series of natural waters are reported in Table III. In each case the fluoride was determined in duplicate.

Table III. Fluoride in Natural Waters

Lab. No.	Sulfate	Blank[a]	Duplicate Determinations					
			Resistance	Ratio	P. p. m. fluoride	Resistance	Ratio	P. p. m. fluoride
	M.E./l.	*Ohms*						
7887	10.8	523	539	1.031	0.40	540	1.033	0.45
7909	12.3	522	537	1.029	0.40	537	1.029	0.40
8031	3.2	522	548	1.050	0.95	548	1.050	0.95
8078	3.0	522	549	1.052	1.0	549	1.052	1.0
8080	2.5	522	526	1.008	0.10	526	1.008	0.10
8090	0.5	522	544	1.042	0.85	543	1.040	0.80
8146	2.0	522	563	1.079	1.7	564	1.080	1.7
8164	2.5	521	549	1.054	1.05	549	1.054	1.05

[a] Resistance, at balance, of a solution of reagents in distilled water.

To test the accuracy of the method, two experiments were undertaken. In the first, the fluoride concentrations of a series of natural waters were determined, then to each of separate aliquots 2 p. p. m. of fluoride were added and the determinations were repeated. The determined values were within ±0.1 p. p. m. of fluoride of the expected value. In the second experiment, a large sample of a natural water was collected. The sample contained 11.6 milligram equivalents per liter of sulfate. Triplicate determinations by the method here described showed 0.40, 0.40, and 0.45 p. p. m. of fluoride. Duplicate aliquots were concentrated and distilled by the hydrofluosilicic acid procedure described by Boruff and Abbott (*2*). The fluoride in these distillates was determined colorimetrically by the procedure here suggested and found to be 0.40 and 0.40 p. p. m. Other aliquots were distilled as above and the fluoride in the distillate titrated with standard thorium nitrate solution following Boruff's procedure (*2*). The result in this case was 0.45 p. p. m. of fluoride. It is concluded, therefore, that the accuracy of the procedure is within ±0.1 p. p. m. of fluoride.

Acknowledgment

The author wishes to express his appreciation to F. N. Cowperthwait, of the Weston Electrical Instrument Corporation, for helpful suggestions, and to Geo. B. Collins, formerly of this laboratory, for assistance in assembling the colorimeter.

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Use of Trichlorobenzene in Analysis of Graphite Greases

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Commercial greases frequently contain chemically inert materials, particularly graphite, from which it is troublesome to separate such ether-insoluble materials as calcium stearate. To carry out the separation for gravimetric determination of graphite, a number of solvents have been compared, some of them differing from the usual types. As a result of this a method for extraction of calcium stearate from graphite by trichlorobenzene has been developed. The method is also applicable to other heavy metal soaps such as aluminum stearate, magnesium stearate, etc., which are even more readily soluble than calcium stearate.

There are given in Table I the series of solvents investigated, their boiling points, and other desirable solubility data. These data show that a number of solvents will dissolve this heavy metal soap, but that in no case is it highly soluble in the cold solvent. The high boiling point of trichlorobenzene, combined with the fact that it is among the better solvents, make it a very satisfactory reagent for such extraction. The following procedure for determination of graphite in greases containing calcium soap is illustrative of its use.

Procedure

Heat 5 grams of the grease with 75 cc. of trichlorobenzene to about 165° C. Centrifugalize while still hot. Decant off the bulk of the trichlorobenzene. Heat the residue with a further quantity of solvent and repeat the operation. Shake the residue with a hot 50 to 50 alcohol-benzene mixture, filter through a tared filter paper, and wash with the same mixture. Dry the residue in the oven and weigh.

If very great accuracy is required, after trichlorobenzene extraction, shake with hot 50 to 50 alcohol-benzene mixture acidified with hydrochloric acid. Filter, and wash well, first with the mixed solvent, then with alcohol, and finally with hot water. Dry and weigh. All filtrations are rapid.

Received February 24, 1934.

Table I. Qualitative Solubility of Calcium Stearate

(0.5 gram of calcium stearate in 10 cc. of solvent)

Solvent	Boiling Point	Solubility[a]		
		At 20°	At 60°	At boiling point
	° *C.*			
Acetone	56	Insoluble	Insoluble	Insoluble
Benzene	80	Moderately	Moderately	Moderately
Butyl alcohol	117	Slightly	Slightly	Soluble but cloudy
Carbon tetrachloride	76	Slightly	Slightly	
Ethylene glycol monoethyl ether	135	Insoluble	Insoluble	Soluble but cloudy
Diethylene glycol	245	Insoluble	Insoluble	Calcium stearate melts clear
				Moderately soluble
o-Dichlorobenzene	179	Slightly	Moderately	Soluble but cloudy
				Separates rapidly on cooling
Isopropyl alcohol	83	Slightly	Slightly	Slightly
Propylene dichloride	97	Insoluble	Insoluble	Slightly
Trichlorobenzene	218	Slightly	Slightly	Completely soluble and clear at 165°
Trichloroethylene	87	Slightly	Slightly	Slightly
Toluene	111	Moderately	Moderately	Moderately
Turpentine	156	Slightly	Moderately	Soluble but cloudy
Xylene	140	Slightly	Moderately	Soluble but cloudy

[a] Slightly soluble, some had dissolved. Moderately soluble, roughly 50 per cent had dissolved.

Determination of Peroxidase Activity

Dean A. Pack,[1] The Birdseye Laboratories, Gloucester, Mass.

THE preservation of fruits and vegetables by freezing and subfreezing temperature storage often requires the inhibition or control of enzyme action. The degree of success with which these measures are applied determines to some extent how well the color, flavor, odor, and other characteristics of the fresh product are retained during storage. A study of these problems has required the adaptation or development of exact methods of determining enzymes applicable to the particular products.

Because of the rather general distribution of peroxidase and the need for control of its activity, a quantitative method of investigation was required. As the Guthrie (*1*) method seemed simple and required no expensive apparatus, it was studied. A preliminary study showed that this method did not give the maximum peroxidase activity of many products—for example, strawberries gave little or no peroxidase activity. This difficulty was corrected in part by thoroughly extracting the enzyme from all the tissue sample and making the determination at the optimum hydrogen-ion concentration for strawberry peroxidase.

The method as now worked out has the advantage of estimating, on a dry-weight basis, the total peroxidase activity of the entire sample in the presence or absence of catalase and at the optimum hydrogen-ion concentration for the peroxidase of the particular product examined.

Experimental Work

The Guthrie method was changed in the following respects:

(1) An extract of the entire tissue sample replaced the pressed juice sample; (2) McIlvaine's dibasic sodium phosphate and citric acid buffer was used instead of sodium hydroxide and citric acid buffer; (3) the reaction of the medium was adjusted to the peroxidase optimum for the particular tissue examined; (4) the amount of all reagents and extracts was reduced 50 per cent, except for toluene which was added as required for complete solution of the indophenol; (5) an enzyme sample in which the peroxidase had been inactivated was added with each reagent blank; and (6) the results were expressed as milligrams of indophenol per decigram of dry substance in the enzyme sample.

In order to obtain maximum peroxidase activity, the samples were ground thoroughly with water or buffer solution and fine sand in a mortar, made up to volume with water or buffer solution, and aliquot samples used for representative determinations. This method gave a more complete extraction of the enzyme than is possible by using only the pressed juice. The point was illustrated by the analyses of two samples of similar tissue and equal weight taken from an individual pear. The peroxidase in samples A was extracted by grinding, while that in samples B was extracted by freezing, thawing, and 5500 pounds pressure per square inch (387 kg. per sq. cm.). The amount of peroxidase in each sample was represented by the milligrams of indophenol produced per decigram of dry weight of samples A and B.

The results are given in Table I for determinations made at both 6.0 and 6.4 pH.

Table I. Peroxidase Activity of Pear Tissue

Sample	Reaction of Mixture, pH	Indophenol Produced[a]
		Mg./dg.
A	6.0	2.76
B	6.0	0.465
A	6.4	3.52
B	6.4	0.604

[a] About 83 per cent of the peroxidase was not in the juice.

While it was noted that the α-naphthol-*p*-phenylenediamine mixture was more sensitive near the neutral point, this sensitivity varied with the kind of buffer used and finally with the compounds used to make up each buffer. Seven different kinds of buffer mixtures were examined. McIlvaine (*2*) and Sorensen (*3*) buffers were found to be less sensitive to the substrate than the other buffers at pH values near the optimum for peroxidase. The magnitude of the complete blanks varied from 20 to 50 per cent of the total indophenol formed, depending upon the kind of enzyme extraction as well as the proximity of the solution to neutrality.

The use of the McIlvaine or the Sorensen citrate–sodium hydroxide buffer mixture made it possible to determine the peroxidase activity at a higher pH value. This modification adds to the usefulness of the method, since it is no longer limited to a reaction of pH 4.5. Table II gives the amount of indophenol produced at the higher and lower pH values by aliquot samples from extracts of various products.

Table II. Effect of Hydrogen-Ion Concentration upon Peroxidase Activity

Product	Sample	Reaction at Optimum pH		Reaction at or near pH 4.5		Catalase Activity of Peroxidase Sample in Oxygen
		pH	Indophenol[a]	pH	Indophenol	
			Mg./dg.		*Mg./dg.*	*Cc.*
Strawberry	1	6.8	1.98	4.5	0.03[b]	0.02
Strawberry	2	6.8	2.33	4.5	0.02[b]	0.02
Pear	3	6.2	4.95	4.5	0.42[b]	0.00
Pear	4	6.2	5.01	4.5	0.45[b]	0.00
Asparagus	5	6.4	113.0	4.4	20.0[a]	1.98
Asparagus	6	6.4	112.2	4.4	21.0[a]	1.98
Potato	7	7.0	60.7	4.4	7.2[a]	0.20

[a] McIlvaine buffer used.
[b] Citric acid and sodium hydroxide buffer used.

These results show that one may substitute the McIlvaine buffer and increase the pH value with an increase of the peroxidase activity. The blanks with the McIlvaine buffers were lower than those with the citric acid and sodium hydroxide buffers.

As the peroxidase of many fruits and vegetables is wholly or partly inactive if determined at pH 4.5, determinations should be made at the optimum pH for the peroxidase being examined. This optimum for strawberries, pears, cauliflower, asparagus, and potatoes was found to be between 6 and 7 pH. One may compare the peroxidase activity of these tissues at the optimum pH values with the activity of the same extracts buffered to a lower pH value (Tables II and III). These results show a notable increase of peroxidase activity at or near the optimum pH value. Peroxidase determinations made by the Willstätter and Stoll method also showed that pear peroxidase was more active at 6.2 than at 4.5 pH.

The catalase in the peroxidase sample may be inactivated at a suitable low temperature with only a slight loss of peroxidase activity. This temperature varies with the product; thus, 60° C. was used for asparagus, while 50° C. was sufficient for pear extracts.

The following experiment was performed to show that pear peroxidase was more active at 6.2 than at 4.5 pH in the absence of catalase:

A 1 per cent chloroform-water extract of pear tissue, having a pH value of 4.56, was heated for 12 minutes at 50° C. to inactivate the catalase. To determine the absence of catalase, samples five times as large as the peroxidase samples were buffered to 6.2 pH and the chloroform was removed from each sample by shaking just previous to the catalase determination. Aliquot samples of this extract, which gave no catalase activity, were used for determination of its peroxidase activity at 6.2 and at 4.5 pH. The McIlvaine buffer was used for the 6.2 pH and the citric acid with sodium hydroxide buffer for the 4.5 pH determinations.

[1] Present address, General Foods Corp., Battle Creek, Mich.

The results given in Table III show that pear peroxidase was also more active at the optimum pH value of 6.2 after the catalase had been destroyed.

Table III. Peroxidase Activity of Pear Tissue after Catalase Had Been Inactivated by Heat

Sample	pH Value of Reaction	Peroxidase Activity (Indophenol Produced)
		Mg.
1	6.2	3.62
2	6.2	3.62
3	6.2	3.69
4	6.2	3.75
5	4.5	0.46
6	4.5	0.44
7	4.5	0.37
8	4.5	0.47

The optimum pH of 6.2 for pear peroxidase was determined experimentally by making peroxidase determinations under controlled conditions and pH values ranging from 4.4 to 8.4. Aside from this, no constant relation has been noted between peroxidase and catalase activity, and it is doubtful if the presence of catalase interferes directly with the peroxidase determination. If this is true, the catalase in peroxidase samples need not be inactivated.

The reagents were used in the same relative proportion as outlined by Guthrie but halved in amount. To insure complete and rapid solution of the indophenol, it seemed best to vary the amount of toluene with amount of indophenol to be dissolved. The indophenol production is linear with the enzyme concentration in dilute solutions. It is best to adjust the enzyme sample so as to not exceed 3 mg. of indophenol per sample.

In order to make the determination of peroxidase comparable, a blank consisting of all reagents and peroxidase-inactivated extract was carried along with each test. The peroxidase in these blanks was inactivated by boiling for 20 minutes just previous to the determination.

The only change in the order of procedure was the addition of the substrate to the enzyme extract and finally the addition of the buffer with the hydrogen peroxide. To avoid part of the sensitivity effect of the reagents, the solutions should be held at a temperature of 25° C. before mixing.

The results were expressed as milligrams of indophenol produced by the peroxidase per decigram of dry substance in the enzyme sample. The dry-weight base was used because the water content of fresh, frozen, and stored frozen products varies considerably.

Procedure Recommended

The suggested procedure for the determination of peroxidase activity is as follows:

Care should be exercised to obtain comparable samples of the product for both dry-weight and peroxidase determinations. The weighed peroxidase sample should be ground thoroughly with fine sand and afterwards made up to a definite volume with water or buffer solution. A measured volume of this enzyme solution is boiled for 20 minutes to destroy the peroxidase and then made up to the measured volume for peroxidase-free samples and indicated as the blank solution. A required volumetric sample of the enzyme solution is placed in a 100-cc. flask and to this are added 6.25 cc. of the substrate solution containing 0.02975 gram of *p*-phenylenediamine hydrochloride in water with 0.595 cc. of 4 per cent α-naphthol in 50 per cent alcohol. (Solutions are made up in these proportions for several samples at one time, brought together, and filtered just before using.) The reaction is started by the addition of 8.75 cc. of a solution containing 6.25 cc. of the optimum pH buffer and 2.5 cc. of 0.05 *N* hydrogen peroxide. The reaction progresses at 25° C. for 10 minutes and is stopped by the addition of 2.5 cc. of a 0.1 per cent aqueous solution of potassium cyanide. A blank determination, made up from all the reagents and the required volume of the blank solution, is carried along with each peroxidase sample. The indophenol produced is dissolved in toluene and separated from the aqueous solution by centrifugalizing for 1 minute. The amount of indophenol in the sample is determined by colorimetric comparison with a standard containing 50 mg. of indophenol per liter of toluene. The amount of indophenol produced by the sample, less that produced by its blank, gives the initial peroxidase activity. From the dry-weight determination, the peroxidase activity is reported as milligrams of indophenol per decigram of dry substance in the peroxidase sample.

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(2) McIlvaine, T. C., *J. Biol. Chem.*, 49, 183–6 (1921).
(3) Sorensen, S. P. L., *Ergebnisse Physiol.*, 12, 393 (1912).

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A Stirrer for Solvent Extraction

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In the extraction by means of immiscible solvents, such as ether-water or carbon tetrachloride–water, the need for intimate contact between the liquid layers is apparent.

Figure 1 shows two modifications of a stirrer designed in this laboratory. When the stirrer is rotated as indicated by the arrows, liquid is drawn from one layer and sprayed in fine droplets through the second phase. In this way intimate contact, with a large interfacial surface, is obtained. This stirrer is particularly advantageous for continuous extractions, since the body of the liquid which is being sprayed is practically undisturbed and may be drawn off continuously during the extraction.

On the left are shown the details of the stirrer used to lift a heavier liquid and spray it through the lighter liquid layer. When the stirrer is rapidly rotated counterclockwise, the movement of the jets, *B-B*, through the liquid cause a decrease in pressure in the hollow shaft of the stirrer. The heavier liquid, into which the open end of the shaft dips, is drawn up into the jets and sprayed through the upper layer. This type of stirrer was designed and successfully used for the treatment of organic liquids with sulfuric acid, where the ratio of acid to organic liquid was very low and uniform treatment was essential.

On the right is shown the modification for downward flow. The principle of operation is the same. In this case the jets, *B-B*, rotate in the heavier liquid, and the lighter solvent is drawn through four small openings, *A-A*, in the upper part of the hollow shaft. This stirrer has been used with entire satisfaction for continuous ether extractions of aqueous solutions. The ether is added continuously below the water surface, the excess ether being drawn off through an overflow.

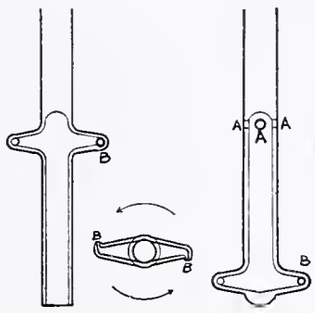

Figure 1

The stirrers used in this laboratory are made from 5-mm. inside diameter glass tubing. The jets are 1 cm. from the center and have about 0.5-mm. openings, turned at right angles to the cross arms (parallel to the direction of rotation). In the down-flow type the openings *A-A* are approximately 1 mm. in diameter.

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Microanalysis of Gaseous Mixtures by Pressure-Temperature Curves

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A micromethod for analysis of gases by pressure-temperature curves, based upon the procedure of N. R. Campbell, has been developed. Less than 1 ml. of sample (N. T. P.) is sufficient for an analysis. The sample is not destroyed and may be reanalyzed. The time required for an analysis is 3 to 5 hours. The only reagent required is liquid nitrogen of which 1 to 2 liters suffice.

The method has been applied successfully to the analysis of synthetic mixtures of pure hydrocarbons, commercial gas samples, and gaseous products obtained in the thermal decomposition of coal in this laboratory.

In those cases where two components form a heterogeneous condensed phase, the determination is simple; if they form a homogeneous condensed phase and have normal boiling points lying close to each other, the determination is more difficult but still possible.

A limitation of the method as developed at the present time lies in the impossibility of determining saturated and unsaturated hydrocarbon gases of the same number of carbon atoms in a mixture. Methods of obviating this difficulty are given.

The method depends on a temperature difference between the evaporation bulb and the balance of the system, and hence can be applied to higher boiling mixtures if suitable pressure-measuring and temperature-control devices are used.

In connection with studies of certain gaseous reactions in this laboratory need was felt for a method for the accurate analysis of small amounts of hydrocarbon gases. Most of the existing methods (*3, 5, 6, 12, 13, 15, 16, 17, 19, 20*) are based on fractional distillation and hence require much larger samples than are available from laboratory experiments. Certain of the existing micromethods (*1, 2, 4, 8, 11, 14*) have not hitherto been applied to the analysis of hydrocarbon mixtures.

A method has been developed which requires a very small sample, less than 1 ml. at normal temperature and pressure, and has been applied satisfactorily to the analysis of synthetic and commercial samples of hydrocarbon gases, as well as to gaseous products obtained in this laboratory from the thermal decomposition of coal. The sample is not destroyed in the procedure and may be reanalyzed, the time required for an analysis is relatively short, and the only reagent required is liquid nitrogen of which a few liters suffice. A limitation of the method at the present time lies in the fact that it has not been found possible to determine saturated and unsaturated hydrocarbons of the same number of carbon atoms in the presence of each other.

The method is a physical one based upon the procedure proposed by Campbell (*4*) and depends upon the characteristic form of vapor pressure–temperature curves. Since the determination of only low-boiling hydrocarbons was desired here, the measurements were made over the range 78° to 298° K. By the use of suitable temperature-control and pressure-measuring devices, the method could be applied to higher boiling substances.

It is usual to plot vapor pressure–temperature curves in linear form, $\log p = 1/T$. If, however, p itself is plotted against the absolute temperature, a graph of the form shown in Figure 1, curve 1, results. From this curve it is evident that, for small values of p, p increases only slightly even with considerable change in T (a to b); then over a certain range there is a rapid change in slope (b to c); this is followed by a sharply rising, nearly linear portion (c to d). The temperature range of rapid change in slope (b to c) was designated by Campbell as "characteristic condensation temperature," but it is, of course, not a single definite temperature. The expression "initial vaporization temperature" (I. V. T.) will be used in this paper to designate this region. Curve 1 (Figure 1) portrays the relations in a closed system of one component when a vapor phase is in equilibrium with its liquid or solid phase. If the system is sufficiently large so that ultimately, owing to increasing temperature, the condensed phase disappears entirely, the curve takes the form shown in Figure 1, curve 2. The first portions of these curves are identical. If T_2 is the temperature at which the condensed phase disappears, the curve from e to f represents merely the expansion of the vapor ($p \propto T$), and, because of the comparatively small rate of change of p with T under such conditions, the change in direction of curve 2 results. If only a relatively small portion of the system undergoes the temperature change—i. e., if the vapor is allowed to expand into a "reservoir" of relatively large volume, maintained at some constant, higher temperature—the portion of the curve from e to f will approach the horizontal. Sharp corners, such as is shown at e, were not experimentally realized, probably owing to adsorption on the walls of the condensing bulb at the relatively low pressures.

If two substances form separate phases in the condensed state, and if their I. V. T.'s are sufficiently far apart so that the more volatile will be relatively completely evaporated from the condensed phase before the vapor pressure of the second becomes appreciable, it is evident that a quantitative determination of the amount of each present can be made by measurements of p and T, and plotting p against T. The pressure-temperature relations in such a system will be as shown in Figure 1, curve 3. The I. V. T.'s, T_3 and T_4, are characteristic of the components, with the exceptions noted later, and hence indicate the qualitative composition; the ratio of p_1 to p_2 gives the fraction by volume of the more volatile component present in the mixture and hence permits calculation of its quantitative composition.

If, as has been found to be the case in the hydrocarbon mixtures worked with in this laboratory, the two substances form one phase in the condensed state, a determination is still pos-

sible in many cases. Now, however, curve *ae* takes the form ae_1, since it is no longer the vapor pressure curve of the more volatile component but is a partial pressure curve of that component, the form of which, in accord with Raoult's law, will be a function not only of the vapor pressure of the more volatile component in the pure state, but also of the concentration of that component in the condensed phase. As a consequence, the values of p for any given temperature will be much lower. It is evident that in such a system, the flat portion of the curve, the period during which there is merely expansion of the vapor of the more volatile component, must be less clearly defined, and may indeed appear merely as a short region of change of slope. It follows that the definiteness of this relatively flat part of the curve, in a system where the substances form a single condensed phase, will be a function of the relative concentration of the components. If the more volatile component is present in great amounts, the flat portion may entirely disappear; if it constitutes only a small fraction of the total, the flat portion becomes more distinct. In some cases a reduction in total pressure was found to be of advantage. This was probably due to the fact that the more volatile component was eliminated from the condensed phase at a lower temperature and hence there was a longer temperature interval for the appearance of the definitive flat portion of the curve, before the I. V. T. of the less volatile component was reached.

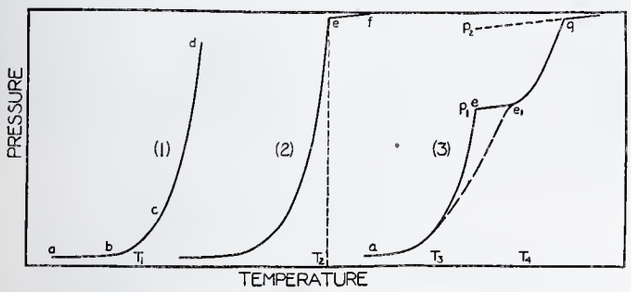

FIGURE 1. IDEALIZED PRESSURE-TEMPERATURE CURVES

In general, I. V. T.'s will be in the same order as the normal boiling points of the substances present. Their value can be approximately determined by plotting p-T curves from published empirical equations, where these cover the necessary low range, but the best method found in this laboratory of fixing these temperatures consists in plotting p-T curves of the pure components from experimentally determined values.

APPARATUS AND METHOD OF OPERATION

The apparatus shown diagrammatically in Figure 2 was constructed of Pyrex glass with no stopcocks or rubber connections in the main system in order to avoid absorption of hydrocarbons by rubber or grease.

The condensation and vaporization of the hydrocarbon gases took place in bulb *C* enclosed in thermostat *A* which was filled with liquid nitrogen to freeze out the condensable gases. Excess liquid nitrogen was drained through the vacuum-jacketed tube connection at the bottom of *A*. It was found that uniformity of temperature in bulb *C* was of the greatest importance in obtaining satisfactory results. To assure this necessary uniformity of temperature, a layer of copper about 1/3 mm. (0.013 inch) thick was deposited electrolytically on the outer surface of *C*, a copper shield was placed around it, and the intervening space, as well as the entire Dewar flask, *A*, was filled with copper turnings. The thermocouple, *B*, was copper-constantan and was in direct contact with the copper coating of bulb *C*. The thermocouple was calibrated at the freezing point of mercury, carbon dioxide sublimation temperature, and boiling point of nitrogen. Good agreement was obtained with accepted values (*18*).

The lower Dewar flask, *D*, was filled with liquid nitrogen and provided with an electric heating coil, *E*, connected in series with a rheostat and an ammeter, which controlled the rate of evaporation of liquid nitrogen and thereby the rate of rise of temperature in thermostat *A*. If, however, the temperature did not increase sufficiently rapidly, a very slow stream of air was blown through the vacuum-jacketed tube connection into *A*. A temperature rise of 0.4° to 0.6° K. per minute was found to be satisfactory.

During an analysis the mercury was raised to a mark on the cut-off, *J*, the apparatus to the right serving only for evacuation of the system and for introduction of the sample. It is essential that the volume of *C*, *F*, and connecting tubing to the mark on *J* be maintained constant, but it is not necessary that either the total volume or the volume of *C* be determined for an analysis. Since almost 95 per cent of the total gas space is not thermostated, it is important that the room temperature be maintained constant within 1° K. to avoid signifieant errors in the pressure readings.

For accurate analyses of mixtures it is important that the pressure be determined for each 2° to 3° K. rise in temperature of bulb *C*, and that the time between corresponding pressure and temperature readings be a minimum. The pressure was determined by means of the McLeod gage *F*. The range was 3×10^{-1} to 1×10^{-8} mm. of mercury. In the first work the McLeod gage was supplied with the usual form of reservoir. It was later found that the special type, as shown at *G*, contributed greatly to the speed and precision of the pressure readings, since by one turn of the control valve, *X*, communication between *F* and *G* was closed, with the result that constant readings of the levels of the mercury columns were obtained at once.

To prepare the apparatus for an analysis, the entire system was first evacuated at room temperature to at least 10^{-5} mm.

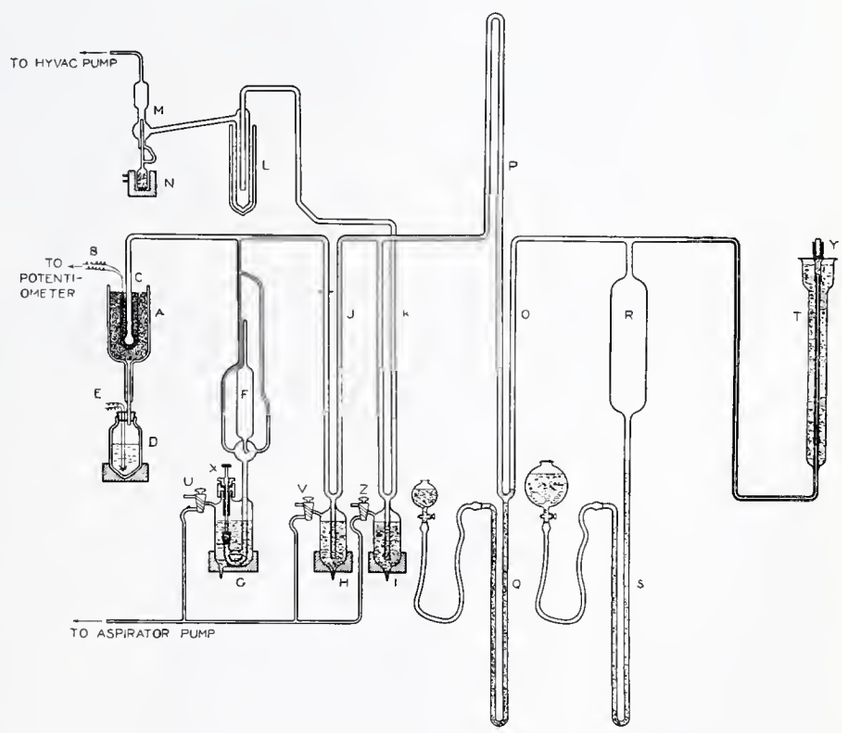

FIGURE 2. APPARATUS FOR MICROANALYSIS OF GASEOUS MIXTURES BY PRESSURE-TEMPERATURE CURVES

A. Dewar flask with vacuum-jacketed tube connection
B. Copper-constantan thermocouple in direct contact with freezing bulb
C. Copper-jacketed freezing tube placed in a 2-mm. (0.079-inch) thick copper shield
D. Lower Dewar flask containing liquid nitrogen
E. Electric heating coil in series with rheostat and ammeter
F. McLeod gage
G, H, I. Mercury reservoirs
J, K, O. Mercury cut-off tubes with mark provided on *J*
L. Liquid nitrogen trap
M. Mercury-vapor pump backed by a Cenco Hyvac oil pump
N. Electric heater
P. Connecting U-tube for introduction of sample
Q, S. Mercury-filled U-tubes in connection with leveling bottles
R. Expansion bulb
T. Sampling reservoir
U, V, Z. Two-way stopcocks for connection with atmosphere or suction
X. Screw attachment connected with stopper for closing communication between reservoir *G* and McLeod gage
Y. Ground-glass stopper provided with cup for holding weights

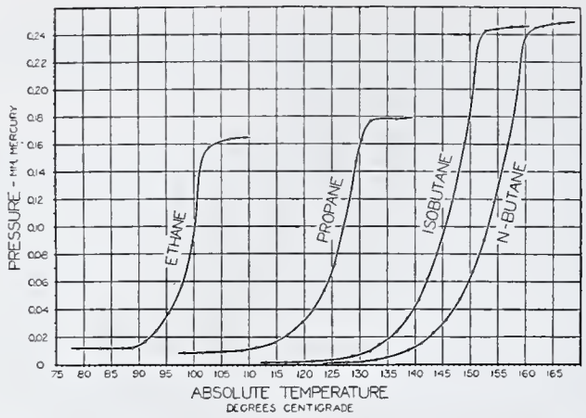

FIGURE 3. VAPOR PRESSURE–TEMPERATURE CURVES OF INDIVIDUAL SATURATED HYDROCARBON GASES

mercury, while the capillary connecting the sampling reservoir, T, with expansion bulb R and cut-off O were completely filled with mercury, and the level of mercury in the right-hand side of P was raised nearly to the top by means of the leveling bottle. A ground-glass stopper, Y, was provided to prevent the mercury from being drawn into the system from T during evacuation. As soon as the level of mercury in P was approximately 760 mm. above the surface in sampling reservoir T, the ground-glass stopper could be removed from the capillary. Before the introduction of the sample the apparatus was shut off from the pump system by partially filling cut-off K with mercury. The sampling tube containing the gas to be analyzed was then slipped over the capillary in T under the surface of the mercury. The sampling tube was pushed down until the capillary end just reached the gas space, and the level of mercury in P was lowered until a few milliliters of gas were drawn above R. The sampling tube was then removed and stopper Y was replaced in position.

In order to introduce the necessary small amount of gas into the evacuated space, the entire sample was drawn into R and expanded to about ten times its volume. As a result the pressure difference in the two sides of the trap was reduced to a few centimeters. Under these conditions the required amount of gas could be transferred to the evacuated space by careful lowering of the leveling bulb in connection with Q. The mercury level was then raised both in O and R. The sample could be stored in this space for any length of time.

The pressure of the gas introduced into the distillation space was usually found to be much higher than that desired. The connection to the pump system was therefore opened, and evacuation continued until the McLeod gage indicated the required pressure, usually of the order of 0.1 mm. of mercury. The mercury level in J was then raised to the mark and kept there throughout the entire analysis. A final pressure measurement was made and recorded as the total pressure, the entire system being at room temperature. Finally, thermostat A was filled with liquid nitrogen from the top. As soon as the temperature of tube C reached that of the liquid nitrogen (78° K.), the pressure of the system was again determined. The residual pressure was a measure of the noncondensable gases. The liquid nitrogen was then drained from the upper thermostat and the temperature was allowed to increase slowly at the desired rate. At intervals of 2° to 3° K. the temperature was recorded and the corresponding pressure measured. In most of the analyses, data were not obtained above 213° K.

If the results of the first analysis do not suffice to indicate definitely the pressures at which a given component has evaporated completely from the condensed phase, the analysis is repeated using slower rates of heating with more frequent pressure readings. Duplicate analyses, under such conditions, were usually found to establish definitely the pressures at which complete evaporation of the various components had taken place.

TABLE I. INITIAL VAPORIZATION TEMPERATURES OF VARIOUS GASES

	Boiling Point °K.	I. V. T. °K.		Boiling Point °K.	I. V. T. °K.
Hydrogen	20.4	....	Carbon dioxide	194.6[a]	110–120
Nitrogen	77.3	....	Propylene	226.1	105–125
Carbon monoxide	81.1	....	Propane	228.6	105–120
Oxygen	90.1	....	Isobutane	262.9	120–133
Methane	111.7	....	n-Butylene	268.1	130–145
Ethylene	169.3	85– 95	n-Butane	279.1	125–140
Ethane	184.8	85–100	Water	373.1	200–220
Acetylene	189.5	85–100			

[a] Sublimation temperature.

SINGLE-COMPONENT SYSTEMS

In order to obtain data for proper interpretation of the pressure-temperature curves of the various mixtures, pressure-temperature curves for individual hydrocarbon gases, of the highest purity obtainable commercially, were made. Figures 3 and 4 show the curves pertaining to the saturated and unsaturated hydrocarbons, respectively. It is evident that such data do not support the assumption of Campbell (*4*) of the existence for each gas of a "characteristic condensation temperature." It is also clear, however, that for all the gases studied there is a range of temperature over which the rate of change of pressure with temperature is relatively rapid. The exact definition of these temperatures is of no practical significance from the standpoint of the method, since, if two components have I. V. T.'s so close as to render their identity uncertain, no separation will be obtained; i. e., the characteristic flat portion of the curve indicating complete evaporation of the more volatile component will never appear. Boiling point and I. V. T. for a number of gases are shown in Table I.

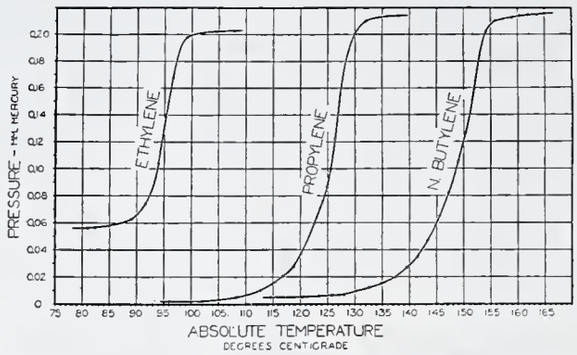

FIGURE 4. VAPOR PRESSURE–TEMPERATURE CURVES OF INDIVIDUAL UNSATURATED HYDROCARBON GASES

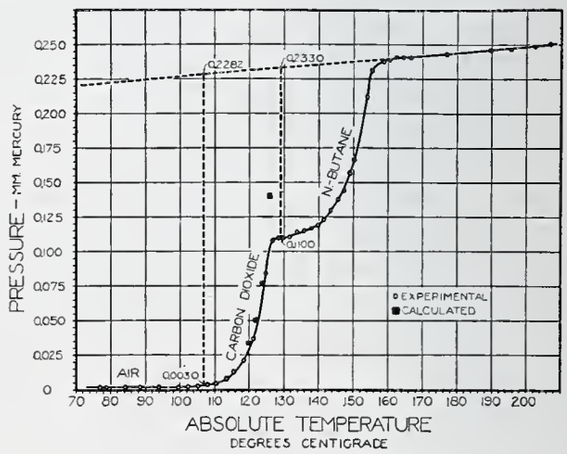

FIGURE 5. GAS MIXTURE 3

	Compn. as Prepared %	Analytical Results: As found %	Analytical Results: On air-free basis %
Carbon dioxide	46.6	45.9	46.5
n-Butane	53.4	52.8	53.5
Air	..	1.3	..
Total	100.0	100.0	100.0

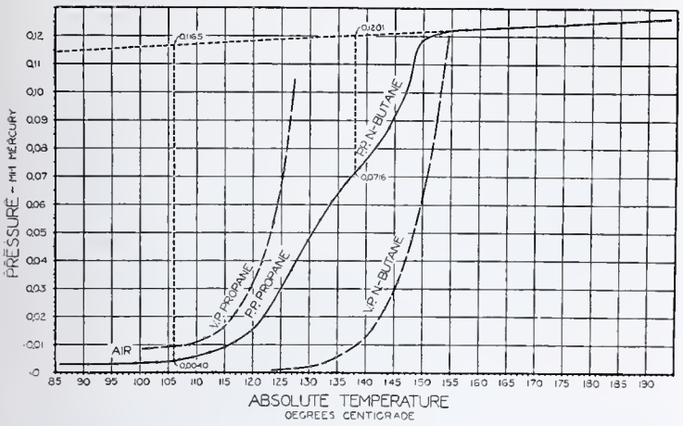

FIGURE 6. GAS MIXTURE 5

	COMPN. AS PREPARED	ANALYTICAL RESULTS
	%	%
Propane	55.9	56.2
n-Butane	40.7	40.4
Air	3.4	3.4
Total	100.0	100.0

It is evident that with liquid nitrogen as a refrigerant no gas with a lower boiling point than ethylene can be condensed and analyzed by this method. All gases with lower boiling points will be found in the noncondensable fraction. In this paper all such noncondensable gases are designated as air, except where methane is known to be present.

TWO-COMPONENT SYSTEMS

HETEROGENEOUS CONDENSED PHASE. In Figure 5 is shown the analysis of a synthetic mixture of carbon dioxide (46.6 per cent) and *n*-butane (53.4 per cent). The total pressure in the system at room temperature was 0.2606 mm. and, after condensation, 0.0015 mm. These small pressures due to noncondensable gases appeared in practically all analyses. The curve shows a rapid change in slope starting at 108° K. and continuing for approximately 12°. The flat portion in the curve, indicating complete evaporation of the carbon dioxide from the condensed phase, appears at a pressure of 0.110 mm. This is the pressure exerted by carbon dioxide plus noncondensable gas, assumed to be air, at this temperature. The volume percentage of carbon dioxide and air in the mixture will be given by the ratio of this pressure to the total pressure of the sample if it could be completely gasified at this temperature. The value for the total pressure which would be exerted by the sample is obtained graphically by a straight-line extrapolation of the *p-T* curve from the temperature at which the sample has completely evaporated down to the temperature in question. Such a straight-line extrapolation is, of course, not exact; however, except at low temperatures the errors introduced by its use have been shown to be negligible by a comparison of the results obtained by the use of this graphical extrapolation with those obtained when the extrapolation was made by the use of pT values for such gases as helium and nitrogen, which had been determined directly in the apparatus. The value for total p so obtained is 0.233 mm. Then $\frac{0.110}{0.233} \times 100$ or 47.2 per cent is carbon dioxide plus air. The butane must be $\frac{0.233 - 0.110}{0.233} \times 100$ or 52.8 per cent. The air is calculated in a similar way, $\frac{0.003}{0.228} \times 100$ and found to be 1.3 per cent.

The combined results are as follows: air 1.3 per cent, carbon dioxide 45.9, and butane 52.8, which are in satisfactory agreement with the composition as prepared. Calculated to an air-free basis, there is even better agreement: carbon dioxide 46.5 per cent, butane 53.5.

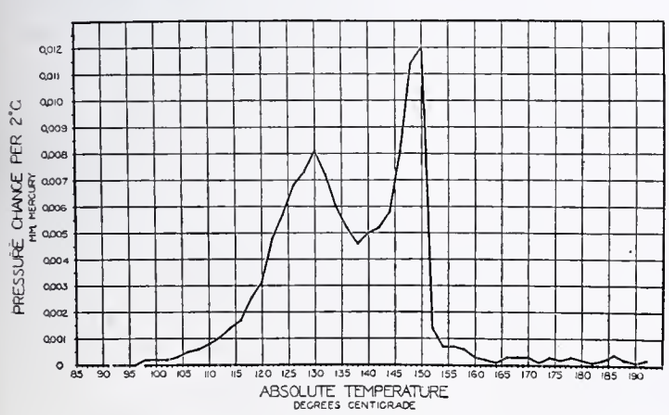

FIGURE 7. DIFFERENTIAL CURVE, GAS MIXTURE 5

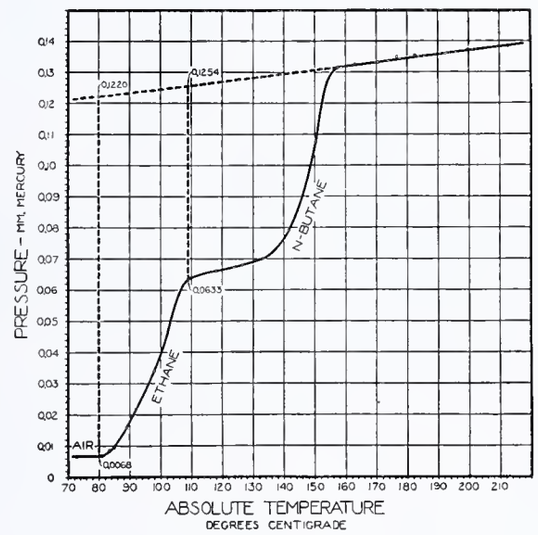

FIGURE 8. GAS MIXTURE 4

	COMPN. AS PREPARED	ANALYTICAL RESULTS As found	ANALYTICAL RESULTS On air-free basis
	%	%	%
Ethane	47.4	44.9	47.6
n-Butane	52.6	49.5	52.4
Air	..	5.6	..
Total	100.0	100.0	100.0

If the classification of this mixture as one in which the condensed material consists of two phases is correct, the value for total pressure at any temperature should be equal to the sum of the vapor pressures of the pure components at that temperature and, since, at those temperatures where the vapor pressure of the carbon dioxide is already considerable, that of the butane is negligible, the curve of total pressures in the system over a certain temperature range should nearly coincide with the vapor pressure of pure carbon dioxide over the same range of temperature. That this is the case is shown by the experimental and calculated values of Figure 5. The values for vapor pressure of carbon dioxide, shown as filled-in circles, were obtained (*9*) from the equation:

$$\log p = -\frac{0.05223 \quad (26179)}{T} + 9.9082$$

HOMOGENEOUS CONDENSED PHASE. In Figure 6 is shown the *p-T* curve for a synthetic mixture consisting of 59.3 per cent propane and 40.7 per cent butane. The vapor pressure curves of the components from Figure 3 are also included. It is evident that the propane contained an appreciable amount of noncondensable gas. The effect of mutual solubility in the condensed phase is clearly shown. The total pressure in the system at any temperature is markedly lower

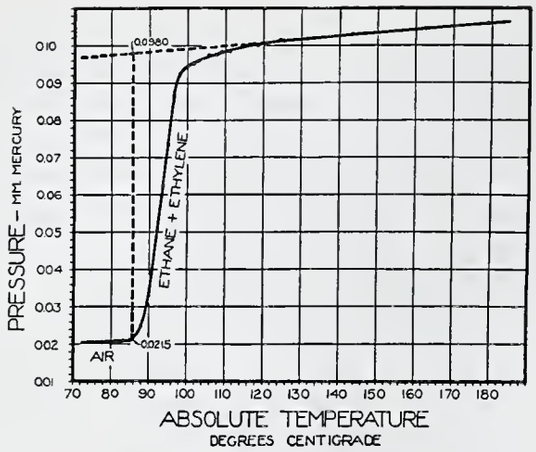

FIGURE 9. GAS MIXTURE 7

	COMPN. AS PREPARED
	%
Ethane	26.7
Ethylene	51.4
Air	21.9
Total	100.0

than the vapor pressure of the more volatile component at that temperature. The effect of solubility in the condensed phase in rendering less evident the flat portion of the curve, where the more volatile component has practically evaporated from the condensed phase, is also well illustrated.

In cases where the pressure at which essentially complete evaporation of the more volatile component from the condensed phase is so poorly defined, recourse may be had to a differential plot as in Figure 7, where the same data shown in Figure 6 are plotted as rate of change per 2° K. against the absolute temperature. The existence of a minimum at 138° K. is clearly evident; hence the choice of 0.0716 mm. as the pressure marking complete evaporation of propane is confirmed. The total pressure in the system at 138° K. if both components were in the gaseous state would be 0.1201 mm. Of this, $\frac{0.0716}{0.1201} \times 100$ or 59.6 per cent is propane plus air and 40.4 per cent butane. The agreement between butane as prepared and as found is satisfactory. There was evidently $\frac{0.0040}{0.1165} \times 100 = 3.4$ per cent of a noncondensable impurity in the propane from which the sample was prepared. Orsat analysis proved this to be air.

In Figure 8 is shown the p-T curve for a synthetic mixture of ethane and butane. Although these two substances also form solid solutions, the flat portion is much more clearly defined because of the much greater difference between their boiling points and, consequently, their I. V. T.'s.

It has been assumed that the flat portions of the p-T curve are indications of the pressures at which the various components are eliminated from the condensed phase. By assuming Raoult's law one can calculate the mole fraction of the more volatile component present, in the condensed phase, at a given temperature. For example,

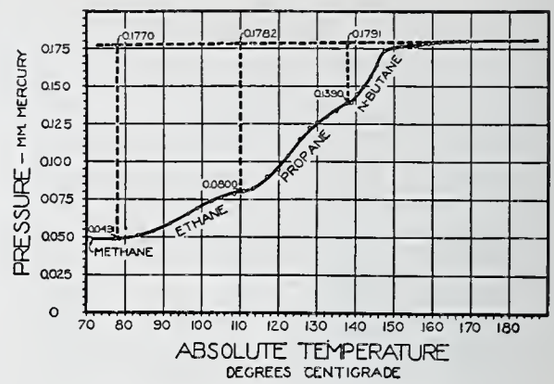

FIGURE 10. GAS MIXTURE 1

	COMPN. AS PREPARED	RESULTS OF ANALYSIS
	%	%
Methane	28.0	27.7
Ethane	17.0	17.2
Propane	32.6	32.7
n-Butane	22.4	22.4
Total	100.0	100.0

in Figure 6 the total pressure at 138° K. is 0.0716 mm. This is made up of the pressure of the air, 0.0056 mm., and of the partial pressures of the propane and butane, but these latter are given by the products of the vapor pressures of the pure gases at 138° K. and their respective mole fractions in the condensed phase. The vapor pressure of propane at 138° K. can be calculated (*10*) from the equation:

$$\log p = -\frac{0.05223\ (19037)}{T} + 7.217$$

$$p = 1.03 \text{ mm. at } 138° \text{ K.}$$

The vapor pressure of butane at the same temperature is found from Figure 3 to be 0.0057 mm. Hence,

$$0.0716 = 0.0056 + 1.03\ M_p + 0.0057\ M_b$$

where M_p, M_b = mole fractions of propane and butane, respectively

since $M_p + M_b = 1$

$M_p = 0.058$

In the original mixture the mole fraction of propane was 0.559 and that of butane 0.407. If x equals the mole fraction of the original propane left in the condensed phase, and if we assume that none of the butane has evaporated (an approximation), then the following relation will hold:

$$\frac{x}{0.407 + x} = 0.058$$

Solving for x we find that 0.0245 is the mole fraction of original propane remaining and hence $\frac{0.559 - 0.0245}{0.559} \times 100$ or 95 per cent of the propane has evaporated.

In the light of the very general character of Raoult's law and the assumption involved in the preceding calculations, the result is considered to be evidence that, even in those cases where the flat portions of the curve are poorly defined, as in the propane-butane mixture (Figure 6), nevertheless they indicate the pressures at which essentially complete

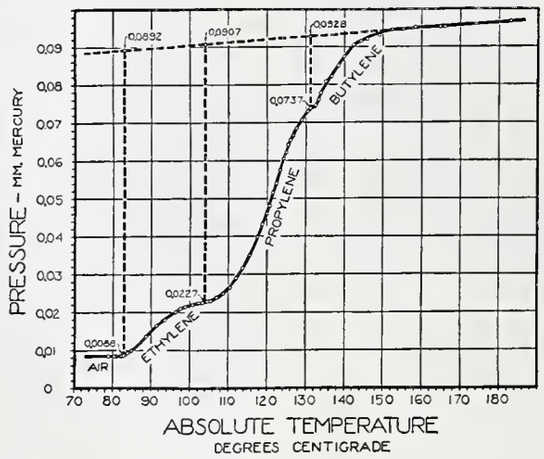

FIGURE 11. GAS MIXTURE 8

	COMPN. AS PREPARED	RESULTS OF ANALYSIS
	%	%
Noncondensable	..	9.8
Ethylene[a]	24.5	15.2
Propylene	54.7	54.4
Butylene	20.8	20.6
Total	100.0	100.0

[a] It is evident from Figure 4 that this component contained considerable amounts of noncondensable impurity, probably air.

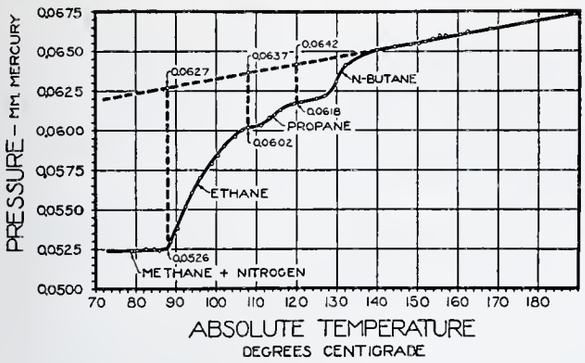

FIGURE 12. COAL DISTILLATION GAS 50

evaporation of a component from the condensed phase has taken place, and that consequently the agreement between the composition as prepared and that found by analysis is not due to compensating factors.

Where the I. V. T.'s overlap or lie close to each other, as in the case of two hydrocarbons such as ethane and ethylene, detection and determination are not possible. This is well illustrated by the curve showing the *p-T* relations in such a mixture (Figure 9). This interference constitutes a definite limitation of the present procedure. It is possible, however, to determine the total unsaturated hydrocarbons in an Orsat apparatus by absorption in bromine water or fuming sulfuric acid, and then to examine the residual saturated hydrocarbons by the method described. In case the composition of the unsaturated hydrocarbon portion is desired, it seems probable that it may be obtained by regeneration of the hydrocarbons from their alkyl bromides (7) followed by a separate analysis on the regenerated unsaturated gases.

SEVERAL-COMPONENT SYSTEMS

Finally, several synthetic gaseous mixtures of three or more components were prepared and analyzed. The method of calculation is essentially the same as that used for two-component systems. An example for four components is presented in Figure 10. The analysis of a mixture of unsaturated hydrocarbon gases is shown in Figure 11.

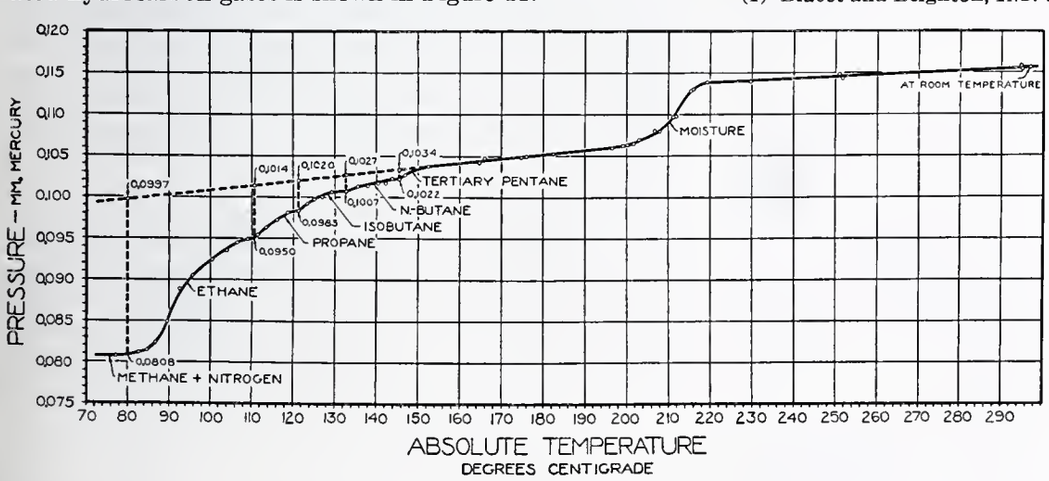

FIGURE 13. NATURAL GAS (CITY GAS OF PITTSBURGH)

APPLICATIONS

The usefulness of the method is illustrated by the following analyses: Figure 12 and Table II, gases from the distillation of bituminous coal; Figure 13 and Table III, Pittsburgh city gas. In these curves the breaks have been attributed to the compounds shown but have not been confirmed in all cases by comparison with synthetic mixtures. In every case the total percentage of hydrocarbons, saturated and unsaturated, was determined by Orsat analysis. In the first two of these analyses the vapor pressure analysis was carried out on a residual sample from the Orsat, from which all constituents had been removed except the saturated hydrocarbons and nitrogen.

TABLE II. ANALYSIS OF GAS SAMPLE 50 OBTAINED FROM CARBONIZATION OF COAL

Av. of three detns.	%
Carbon dioxide	1.82
Unsatd. hydrocarbons	0.88
Oxygen	1.00
Hydrogen	48.00
Carbon monoxide	2.96
Total satd. hydrocarbons	35.54
Nitrogen	9.80
Total	100.00

By the conventional assumption that the satd. hydrocarbons consist of $CH_4 + C_2H_6$ only:

Methane, %	27.26
Ethane, %	8.28
	35.54

Av. weighted empirical formula of satd. hydrocarbons calcd. from the combustion data, $CH_{3.62}$

COMPOSITION OF SATURATED HYDROCARBONS

	I	II	III	Av.
	%	%	%	%
Methane	28.45	28.23	28.39	28.36
Ethane	4.36	4.81	4.76	4.64
Propane	1.68	0.80	0.87	1.12
n-Butane	1.05	1.70	1.52	1.42
Total	35.54	35.54	35.54	35.54

Av. weighted empirical formula calcd. for total satd. hydrocarbons. $CH_{3.74}$.

TABLE III. ANALYSIS OF SAMPLE OF PITTSBURGH CITY GAS

(January 24, 1933)

Av. of three detns.	%
Carbon dioxide	Nil
Unsatd. hydrocarbons	0.88
Oxygen	0.24
Hydrogen	Nil
Carbon monoxide	Nil
Total satd. hydrocarbons	89.63
Nitrogen	9.25
Total	100.00

By the conventional assumption that the satd. hydrocarbons consist of $CH_4 + C_2H_6$ only:

Methane, %	78.63
Ethane, %	11.00
	89.63

Av. weighted empirical formula of satd. hydrocarbons calcd. from combustion data, $CH_{3.7}$

COMPOSITION OF SATURATED HYDROCARBONS

	I	II	Av.
	%	%	%
Methane	71.06	70.87	70.97
Ethane	12.05	12.52	12.28
Propane	2.94	2.62	2.78
Isobutane	1.37	1.69	1.53
n-Butane	1.25	0.78	1.01
tert-Pentane	0.96	1.15	1.06
Total	89.63	89.63	89.63

Av. weighted empirical formula calcd. for total satd. hydrocarbons, $CH_{3.75}$

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Turbidity in Sugar Products

II. Effect of Independent Variation of Suspended and Coloring Matter on Transmittancy and Tyndall Beam Intensity

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Equations have been derived and graphs constructed for two systems containing both coloring matter and turbidity, by means of which their concentration can be derived from measurements of transmittancy and Tyndall beam intensity.

In the two fairly closely related systems—Filter-Cel plus caramel solution, and unfiltered plus filtered sugar sirups—the relationships between color and turbidity concentration on the one hand and transmittancy and Tyndall beam intensity on the other have been found not to be identical. Consequently, a simplified mathematical treatment of the problem of determining turbidity and color in the presence of each other must be confined to the particular system which is being studied, and specific relationships which hold for one case cannot be applied indiscriminately to any other system. Photometric determinations are undoubtedly to be preferred to mere comparisons with empirical standards.

The first paper of this series (*8*) dealt with the transmittancy and Tyndall beam intensity of a raw sugar solution at varying depth of layer, and at varying concentration obtained by dilution with a clear, colorless sugar sirup. The proportion between suspended matter and molecularly dispersed coloring matter remained always the same. Under these circumstances the ratio between the Tyndall beam intensity and the transmittancy is, within a limited range, a power function of the depth or of the concentration of total light-absorbing material.

The various products of the sugar house present a much more complicated problem, because here coloring matter and suspended matter vary independently of each other. Furthermore, the size and shape of the suspended particles and their light-absorbing and reflecting properties may vary not only from one product to another, but also for one and the same product through coagulation or peptization produced by mechanical effects or by the mere time factor.

Even if the characteristics of the particles and the possibilities of change in them be left out of consideration, no general theory of the transmittancy and Tyndall beam intensity of systems containing both suspended and coloring matter in varying proportions has as yet been developed, previous work having been confined principally to suspensions in colorless media where absorption is due solely to the suspended matter. Cummins and Badollet (*2*) have recently reported measurements of Tyndall beam intensities in sugar products and other colored media; but while they imply that the presence of coloring matter affects the readings obtained, they do not specify how the necessary corrections may be made.

Formulas covering suspensions in colorless media, and assuming perfectly diffused light, have been established by Wells (*7*) on the basis of the theory of Channon, Renwick, and Storr. Wells shows that in such systems the optical density ($-\log T$) is not directly proportional to the depth or the concentration (Lambert-Beer law), but increases more slowly than either, because part of the incident light is lost by reflection or scattering. The rigorous equations are rather involved, but for limited ranges, and well within the limits of experimental error, the optical density increases linearly with a power function of the depth, the exponent being less than unity. The Tyndall beam intensity is an even more complex function of the depth or concentration of suspensions in colorless media. Wells gives a complete formula for that relationship, but it contains eight constants and is too cumbersome to use in practice. Within limited ranges the simpler power formula, which applies to the optical density, affords in this case also close approximations to the experimental data.

Sauer (*5*) has derived certain formulas which are applicable to suspensions in colorless media, particularly for the Pulfrich photometer. According to him, if the absorption is so small as to be negligible, the Tyndall intensity is directly proportional to the thickness. If the absorption is considerable, it may be corrected for by applying a factor based on the optical density. Sauer states that the absorption due to coloring matter in true solution is usually slight in comparison to that caused by the suspended particles, and that if the cell thickness is properly chosen so that the absorption becomes negligible, the observed Tyndall beam intensity will vary directly with the total number of suspended particles. Even if the coloring matter caused considerable absorption, it should be possible, according to Sauer, to apply a correction factor. The writers' experience has shown, however, that such a simple procedure cannot be used in the case of systems like sugar products, where the absorption due to coloring matter is very high and where multiple reflection is a further disturbing factor.

The wide gap existing between the systems which have received mathematical treatment and those with which the writers have to deal required bridging. Experiments were therefore undertaken to measure the transmittancy and Tyndall beam intensity of turbid, colored solutions of known composition, in order to ascertain the practical applicability of this method for the measurement of turbidity and of color.

Series A. Bentonite and Caramel

In similar investigations Lindfors (*4*) and Balch (*1*) used bentonite to produce turbidity, and caramel as the coloring matter. The writers adopted these same materials in the first series of their experiments. Systems of this nature present great difficulties in technic, because of their instability. After considerable preliminary work a sufficiently stable turbid medium was prepared by suspending bentonite in a solution of gum acacia, which acted as a protective colloid.

The coloring matter was prepared according to Ehrlich's method (*3*) from Domino tablet sugar, by heating the powdered substance *in vacuo* in an oil bath at 200° C. and holding it at that temperature for one hour after all frothing had ceased.

One hundred grams of the caramel thus obtained were ground to a fine powder and dissolved in 200 cc. of distilled water. The solution was treated with 5 grams of x-ray grade of barium sulfate, shaken thoroughly with it, and filtered by suction through acid-washed asbestos on a Jena fritted glass funnel. The filtration was repeated ten times through the same pad, and the final filtrate was collected in a clean, dry filter flask. This caramel solution was found, on subsequent test, to be as free of suspended matter as freshly distilled water.

To prepare the mixtures containing specified quantities of turbid and coloring matter, the stock bottles of bentonite suspension and caramel were vigorously shaken and placed in a water bath held at 20° C. When the contents had reached 20° C. the caramel solution was placed dropwise in a series of 25-ml. volumetric flasks, from a 5-cc. microburet with a ground tip. The desired amount of bentonite suspension was then added from a graduated pipet, the stock bottle being well shaken before each removal. The mixture of bentonite suspension and caramel solution was diluted with distilled water nearly to the mark, and the volume finally adjusted at 20° C.

The photometer readings were taken after less than 2 hours. The flasks were slowly rotated for mixing. Even this gentle treatment seriously affects the Tyndall intensity readings, and for this reason the transmittancies were determined first, as these are only slightly affected. Thorough mixing is essential for the Tyndall measurements, but the suspensions must not be agitated vigorously. The cells were rinsed four times with the solution in order to insure complete removal of previously contained material. The cover of the cell was put in place, and the cell carefully washed with distilled water, dried, and polished. Special care must be taken to insure optically perfect cell walls.

Standardization of technic was found to be of paramount importance. Equal timing of similar operations, uniform rate of mixing, and the most scrupulous maintenance of comparable experimental conditions are mandatory if any significance is to be attached to any of the observed readings.

Thirty-five different mixtures of suspended and coloring matter were prepared, the bentonite concentration being varied in five steps and the caramel concentration for each of these suspensions in seven steps. The transmittancy and Tyndall beam intensity of all the mixtures were determined with the Pulfrich photometer (*8*) in a 5.09-mm. cell, under the green and red filters—that is, at effective wave lengths of 529 and 621 mμ, respectively.

On the basis of these measurements the mathematical relationships between the transmittancy and the Tyndall beam intensity on the one hand, and the concentration of coloring matter and turbidity on the other, were formulated, and the constants in the formulas evaluated for a number of typical cases. The results proved that the particular kind of bentonite used had an adsorptive effect on the caramel, and that for this reason the concentrations of suspended and coloring matter in the mixtures on which the observations were made, were different from those before mixing. Although the findings are of considerable interest from the standpoint of adsorption equilibria, they do not furnish a solution of the present problem, and the results are therefore omitted here.

It is evident that when Lindfors' method of preparing bentonite-caramel standards is used, it must first be ascertained whether or not the particular bentonite adsorbs caramel; if it does, the standards will be valueless.

Series B. Filter-Cel and Caramel

Experiments were next undertaken with Filter-Cel purified by acid washing and fractional sedimentation. The Filter-Cel suspension and caramel solution were prepared in the same manner as the corresponding materials in Series A. The transmittancies and Tyndall beam intensities of these mixtures were measured as described above, with the results shown in Tables I and II.

The relations between the transmittancy and Tyndall beam intensity on the one hand, and the concentration of turbidity and coloring matter on the other were now analyzed separately. The following symbols are used in this discussion:

N = cc. of bentonite suspension (concentration of turbidity)
C = drops of caramel solution (concentration of coloring matter)
T = per cent transmittancy
D = optical density ($-\log T$)
R = Tyndall beam intensity, in per cent of standard block[1]

Table I. Transmittancies of Filter-Cel-Caramel Mixtures

Drops of Caramel	Filter-Cel Suspension 0 cc.	4 cc.	8 cc.	12 cc.	16 cc.	20 cc.	24 cc.
	Red filter, 5.09-mm. cell						
0	100.00	98.42	82.18	80.58	76.39	72.70	65.14
4	99.02	88.28	81.78	76.80	68.18	65.72	63.36
8	90.90	84.62	77.96	71.96	67.14	64.58	59.75
12	89.58	79.20	75.02	67.39	63.99	61.07	57.95
16	81.82	74.56	70.64	64.26	60.91	57.11	54.79
20	76.68	73.28	66.76	58.73	58.06	54.18	50.75
	Green filter, 5.09-mm. cell						
0	100.00	91.80	78.21	75.04	69.95	65.58	58.60
4	87.62	77.42	68.31	62.87	55.62	52.91	51.10
8	72.68	65.96	58.95	53.24	49.82	46.52	43.28
12	63.28	54.88	49.47	45.73	42.49	39.37	36.90
16	52.17	44.51	42.78	39.29	35.57	33.19	31.38
20	42.92	40.58	36.16	30.86	29.92	28.75	25.54

Table II. Tyndall Intensities of Filter-Cel-Caramel Mixtures

Drops of Caramel	Filter-Cel Suspension 0 cc.	4 cc.	8 cc.	12 cc.	16 cc.	20 cc.	24 cc.
	Red filter, 5.09-mm. cell						
0	50	1462	3254	4190	4979	5338	7118
4	114	1387	3098	4140	5267	6022	6379
8	103	1256	2842	3862	4807	5692	5972
12	136	1295	2427	3698	4639	5492	5933
16	200	1217	2341	3190	4489	4538	5476
20	122	989	2185	3069	4354	3923	5568
	Green filter, 5.09-mm. cell						
0	18	465	1123	1513	1792	1947	2302
4	36	413	962	1284	1562	1701	1877
8	26	305	751	1030	1262	1437	1478
12	32	264	502	842	1131	1182	1284
16	36	188	438	530	913	950	1060
20	24	155	361	448	779	517	1065

Transmittancy. An examination of the transmittancy figures showed that when turbidity is constant and coloring matter varies, the optical density is directly proportional to the color concentration—i. e., that Beer's law holds for the coloring matter, irrespective of the turbidity present simultaneously. Expressed in a formula,

$$-\log T = c\,C, \text{ or } C = \frac{-\log T}{c} \qquad (1)$$

Under the red filter $c = 0.00590$, and under the green filter 0.018075.

Balch had previously found that Beer's law does not apply for varying turbidity at constant color, and the writers pointed out (*8*) that Balch's results satisfy a power formula. This has been confirmed in the present series of experiments. The formula is as follows:

$$N = kD^n, \text{ or } D = \left(\frac{N}{K}\right)^{\frac{1}{n}} \qquad (2)$$

For the particular system investigated the numerical value of the constants is:

	Red Filter	Green Filter
n	1.188	1.232
$\log k$	2.24645	2.17266

[1] The absolute Tyndall beam intensity of standard block 323, used by the writers, is reported by Zeiss to equal 0.00282 of the intensity of the incident light, for the green screen, under the experimental conditions of the Pulfrich photometer. Corresponding figures for the blue and red screens have not been furnished. To calculate the absolute Tyndall beam intensity of a solution, 0.01 R is multiplied by the absolute intensity of the standard block for the same screen, and the product multiplied by a factor which varies with the vessel used as the container for the solution. For a 2.5-mm. plane parallel cell this factor is 6.5.

The absorptions due to the coloring matter and to the turbidity are additive, and the combined formula may therefore be written

$$-\log T = cC + \left(\frac{N}{k}\right)^{\frac{1}{n}} \qquad (3)$$

When the values for C, N, c, k, and n are substituted in this formula, the transmittancies given in Table III are obtained.

Table III. Calculated Values of T for Stated Values of C and N

Values of C	Values of N: 0	4	8	12	16	20	24
			Red filter				
0	100.0	90.9	84.3	78.7	73.7	69.2	65.1
4	94.7	86.1	79.9	74.5	69.8	65.5	61.6
8	89.7	81.6	75.6	70.6	66.1	62.1	58.4
12	85.0	77.2	71.6	66.8	62.6	58.8	55.3
16	80.5	73.2	67.9	63.3	59.3	55.7	52.4
20	76.2	69.3	64.3	60.0	56.1	52.7	49.6
			Green filter				
0	100.0	88.5	80.7	74.2	68.6	63.7	59.2
4	84.7	74.9	68.3	62.8	58.1	53.9	50.2
8	71.7	63.4	57.8	53.2	49.2	45.6	42.5
12	60.7	53.7	49.0	45.0	41.6	38.6	36.0
16	51.4	45.5	41.5	38.1	35.3	32.7	30.4
20	43.5	38.5	35.1	32.3	29.8	27.7	25.8

Considering the experimental difficulties and possibilities of shifts in the colloid equilibrium during observations, the agreement between found and calculated values is good for the green filter. For the red filter the figures do not check so well, owing to the disturbing differences in tint in the two halves of the field.

The results show that no adsorption of caramel by the Filter-Cel took place, because in every case the ratio between the transmittancy of the turbid colored solution and that of the corresponding colored solution free from turbidity was the same as the ratio between the transmittancy of the turbid colorless solution and that of water. This is the rule which Balch (*1*) had previously found to hold when there is no adsorption.

Tyndall Beam Intensity. An examination of Table II shows that the Tyndall beam intensity increases with the turbidity at each color concentration.

With the turbidity constant and color varying, irregular figures are obtained at turbidity 0, due to small and unavoidable admixture of turbidity. At turbidities above 4, increasing color generally causes a decrease in the Tyndall intensity. As in the bentonite-caramel series, where the intensity first increased and then decreased, a few of the figures in Table II, between colors 0 and 4 under the red filter, show a tendency to rise, but above color 4 the maximum of the curve has evidently been passed.

Between the limits of turbidity from 4 up to 24 and of color from 4 up to 20, the Tyndall beam intensity is, at constant color concentration, an approximately linear function of the log of the turbidity concentration, according to the formula

$$R = a \log N - k \qquad (4)$$

The values of the constants a and k were found to be

Color	Green Filter a	Green Filter k	Red Filter a	Red Filter k
4	1880	725	6189	2291
8	1488	573	5649	2101
12	1178	453	5156	1926
16	932	358	4706	1766
20	738	283	4295	1619

Both a and k are functions of the color concentration C:

$$a = b\,d^{-C}$$
$$k = c\,f^{-C}, \text{ or}$$
$$\log a = \log b - (\log d)\,C$$
$$\log k = \log e - (\log f)\,C$$

The equation for R, as a function of C and N, may thus be written

$$R = b\,d^{-C} \log N - ef^{-C} \qquad (5)$$

The numerical values for log b, log d, log e, and log f in this particular system are

	Green Filter	Red Filter
log b	3.37569	3.83130
log d	0.025382	0.009915
log e	2.96248	3.39673
log f	0.025535	0.009175

The values of a and k cannot be extrapolated to zero color. With no coloring matter present, the values of log a and log k are

	Green Filter	Red Filter
log a	3.33786	3.79302
log k	2.92840	3.37566

If the values of a and k shown above are substituted in formula 4, the figures given in Table IV are obtained.

Table IV. Calculated Values of R, for Stated Values of C and N

Values of C	Values of N: 4	8	12	16	20	24
			Green filter			
0	463	1118	1501	1773	1980	2157
4	407	973	1314	1539	1721	1870
8	323	771	1033	1219	1363	1481
12	256	611	818	965	1079	1173
16	203	484	648	765	853	929
20	161	383	513	606	677	736
			Red filter			
0	1363	3232	4326	5101	5703	6195
4	1435	3298	4388	5161	5761	6251
8	1300	3001	3995	4701	5248	5696
12	1178	2730	3638	4280	4782	5190
16	1067	2484	3313	3900	4356	4729
20	967	2260	3016	3553	3969	4309

Under the green filter, the agreement between calculated and found values is satisfactory, except where the experimental values are obviously out of line as shown by a direct comparison of found values with those adjacent in different directions. Under the red filter, the agreement is not nearly as good as under the green, for the same reason as given in the discussion of the transmittancy figures. In both spectral regions the agreement is less good at high turbidity and high color. Here multiple reflection appears to become more pronounced, and this is probably one reason for the observed deviations.

By means of formulas 3 and 5 above, C and N in unknown mixtures of the caramel and Filter-Cel used in this series may be calculated after T and R have been determined, but the result may be ascertained more quickly and easily by means of a graph.

Series C. Mixtures of Sugar Sirups

The next step in this investigation was to ascertain whether the relationships found for the Filter-Cel and caramel mixtures would also hold in the case of actual sugar products.

This problem was attacked by selecting a very dark raw sugar containing a large quantity of suspended matter, dissolving it to a sirup of 60° Brix, and removing coarse suspended matter by vacuum filtration through 250-mesh bronze gauze. Part of this sirup was carefully filtered through purified Filter-Cel and asbestos to free it as far as possible of suspended matter. A white sugar sirup was prepared from Domino sugar tablets, decolorized with Suchar, and filtered like the raw sugar sirup. All three sirups were finally adjusted again to 60° Brix by refractometer. Solutions containing varying proportions of coloring matter and turbidity were then made by weighing and mixing the three sirups in proportions of 0 to 5 parts of each.

If one part of unfiltered raw sugar sirup represents one unit of coloring matter (C) and one unit of turbidity (N), then

one part of filtered raw sugar sirup equals one unit of coloring matter plus a small amount of residual turbidity not removed by filtration, and one part of filtered white sirup represents zero color plus a small amount of residual turbidity.

The transmittancy and Tyndall beam intensity of all the mixtures were determined under three color screens, blue (449 mμ), green (529 mμ), and red (621 mμ), in a 2.5-mm. cell. The results of these measurements are shown in Table V, where U indicates one part of unfiltered raw sugar sirup, F one part of filtered raw sugar sirup, and W one part of filtered white sirup.

Table V. Transmittancies and Tyndall Beam Intensities of Sirup Mixtures

Mixtures	Transmittancy			Tyndall Beam Intensity		
5 C units	Blue	Green	Red	Blue	Green	Red
5 U, 0 F, 0 W	2.15	11.40	29.25	59.34	913.3	5914
4 U, 1 F, 0 W	3.27	13.97	33.53	52.38	799.1	5117
3 U, 2 F, 0 W	4.23	17.17	40.50	35.95	492.9	3765
2 U, 3 F, 0 W	5.97	22.17	46.35	29.15	367.8	2376
1 U, 4 F, 0 W	7.87	26.87	54.25	19.04	194.5	1345
0 U, 5 F, 0 W	10.37	35.22	66.27	5.67	51.24	260.4
4 C units						
4 U, 0 F, 1 W	4.77	17.10	36.70	75.12	898.5	4925
3 U, 1 F, 1 W	5.93	21.40	42.92	59.12	600.8	3961
2 U, 2 F, 1 W	8.18	26.37	50.73	44.72	441.2	2816
1 U, 3 F, 1 W	11.93	33.08	60.47	30.03	274.4	1444
0 U, 4 F, 1 W	16.00	43.30	72.37	7.32	60.51	210.3
3 C units						
3 U, 0 F, 2 W	9.80	26.42	47.30	106.7	917.1	4187
2 U, 1 F, 2 W	13.33	33.92	55.30	81.2	592.9	3259
1 U, 2 F, 2 W	17.70	42.07	65.28	51.4	330.9	1708
0 U, 3 F, 2 W	24.45	53.17	77.85	12.9	90.3	333.8
2 C units						
2 U, 0 F, 3 W	21.07	42.33	60.62	128.9	863.8	3340
1 U, 1 F, 3 W	27.43	49.03	71.93	74.13	396.8	1641
0 U, 2 F, 3 W	40.23	64.87	83.05	10.91	55.08	208.5
1 C unit						
1 U, 0 F, 4 W	44.90	64.35	78.45	124.4	480.6	1737
0 U, 1 F, 4 W	62.03	80.50	90.62	14.03	54.15	160.7
0 C unit						
0 U, 0 F, 5 W	100.00	100.00	100.00	6.83	21.55	74.61

A preliminary examination of the transmittancy figures in Table V showed that at constant F each unit of U-W increases $-\log T$ by a constant amount, within the limits of error, and that the same is true for each unit of F-W at constant U. In other words, Beer's law appears to hold for both color and turbidity. The $-\log T$ increment for U-W is due to 1 C plus 1 N minus the residual turbidity in the filtered white sirup, while that for F-W represents 1 C plus the residual turbidity in the filtered raw sugar sirup minus the residual turbidity in the filtered white sirup.

In order to find the transmittancies for 1 C and 1 N, it is necessary to apply corrections for the residual turbidity in both filtered sirups. These corrections cannot be found from the transmittancy figures, because in the filtered raw sugar sirup the absorption effect of suspended and of coloring matter cannot be separately determined by this means, and because the white sugar sirup showed zero turbidity by the transmittancy method although the Tyndall beam method revealed measurable turbidity. Therefore the necessary corrections had to be derived from the Tyndall beam intensities.

Tyndall Beam Intensity. A glance at Table V shows that at constant color concentration there is an approximately linear relationship between parts of turbid sirup ($U = N$) and the Tyndall beam intensity under the green and red screens, but this relationship is obscured by the effect of the residual turbidity in the other two sirups, and more so under the blue screen.

In order to test this hypothesis of linear relationship between R and N, the values of R corresponding to one unit each of U, F, and W were calculated by the method of least squares from the experimental data given in Table V. In the series with 5 color units there are 6 equations, with two unknowns; in the series with 4, 3, and 2 color units there are 5, 4, and 3 equations, respectively, with three unknowns, but since the quantity of filtered white sirup was constant at each individual color concentration, a value for W, known to be small, had to be assumed as a first approximation. Two sets of equations were therefore set up, in one of which the turbidity in W was assumed to be zero, and in the other equivalent to one-third of that in F. The results of these two sets of equations showed that within these limits the value for W had little effect on the values of R corresponding to U and of F, which came out very nearly the same.

From these data formula 6 was derived, and this made it possible to calculate the values of R corresponding to 1 W at color concentrations 1, 2, 3, and 4, from that found experimentally at zero color concentration. With R for 1 W known, the R values of U and F at each color concentration could now be readjusted, and the final results of the calculations are shown in Table VI.

Table VI. Values of R, for One Unit of U, F, and W

	Blue	Green	Red
5 C units			
U	11.94	183.2	1211
F	1.75	4.7	40.6
W	0	0	0
4 C units			
U	19.05	213.9	1265
F	2.60	13.64	70.4
W	0.14	1.68	10.7
3 C units			
U	36.57	298.0	1446
F	5.45	23.8	135
W	0.25	2.13	11.64
2 C units			
U	65.1	421.4	1672
F	6.15	17.0	81.7
W	0.43	2.69	12.64
1 C unit			
U	121.3	467.0	1682
F	10.95	40.5	105.7
W	0.77	3.41	13.74
0 C unit			
W	1.37	4.31	14.92

Simple addition of the R values for U, F, and W shown in Table VI results in the R figures given in Table VII, representing the adjusted values of the Tyndall beam intensities for the sirup mixtures. The corresponding values of N are also presented, calculated by dividing the R values for the mixtures by the corresponding R values for 1 U (equivalent to 1 N), as given in Table VI.

Table VII. Adjusted Tyndall Beam Intensity and Turbidity Concentration Values of Mixtures Listed in Table V

Mixtures	Tyndall Beam Intensity (R)			Turbidity Concentration (N)		
5 C units	Blue	Green	Red	Blue	Green	Red
$5U + 0F + 0W$	59.7	916	6055	5.000	5.000	5.000
$4U + 1F + 0W$	49.5	738	4885	4.147	4.026	4.034
$3U + 2F + 0W$	39.3	559	3714	3.293	3.051	3.067
$2U + 3F + 0W$	29.2	381	2544	2.440	2.077	2.101
$1U + 4F + 0W$	18.9	202	1374	1.586	1.103	1.134
$0U + 5F + 0W$	8.8	23.5	203	0.733	0.128	0.168
4 C units						
$4U + 0F + 1W$	76.3	857	5071	4.007	4.008	4.009
$3U + 1F + 1W$	59.9	657	3876	3.144	3.071	3.065
$2U + 2F + 1W$	43.4	457	2692	2.280	2.133	2.120
$1U + 3F + 1W$	27.0	257	1487	1.417	1.196	1.176
$0U + 4F + 1W$	10.5	69.9	293	0.553	0.258	0.232
3 C units						
$3U + 0F + 2W$	110.2	898	4350	3.013	3.013	3.016
$2U + 1F + 2W$	79.1	624	3039	2.163	2.094	2.109
$1U + 2F + 2W$	48.0	350	1728	1.312	1.174	1.203
$0U + 3F + 2W$	16.9	75.7	417	0.461	0.254	0.296
2 C units						
$2U + 0F + 3W$	131.5	851	3382	2.020	2.019	2.023
$1U + 1F + 3W$	72.6	447	1692	1.114	1.060	1.072
$0U + 2F + 3W$	13.6	42.1	201	0.209	0.100	0.120
1 C unit						
$1U + 0F + 4W$	124.4	481	1737	1.026	1.029	1.033
$0U + 1F + 4W$	14.1	54.1	161	0.128	0.116	0.096
0 C unit						
$0U + 0F + 5W$	6.85	21.6	74.6	0.033	0.036	0.040

A comparison of the R values given in Table VII with those found experimentally (Table V) shows that the assumed linear relationship between N and R, at constant color concentration, actually holds. The deviations are partly due to experimental error, because it is very difficult to prepare

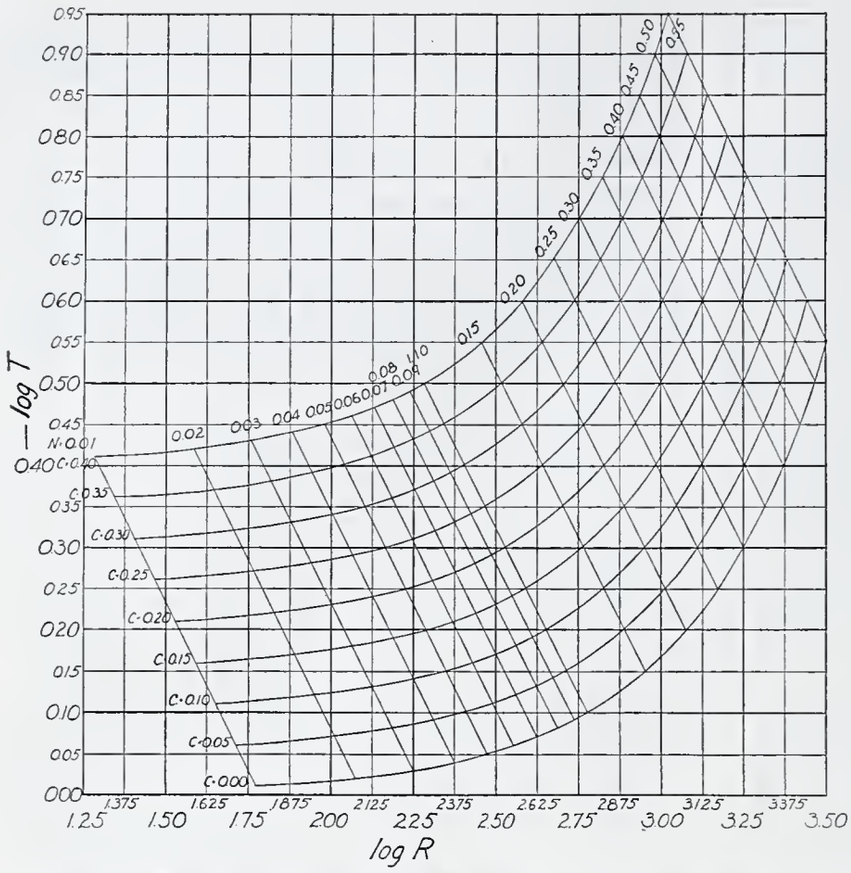

Figure 1. Negative Log of Transmittancy and Log of Tyndall Beam Intensity, Corresponding to Varying Concentrations of Coloring Matter and Turbidity Expressed as Negative Logs of Transmittancy

homogeneous mixtures of these heavy sirups. Another reason is that the suspended particles remaining after filtration are probably different in size from those filtered out. The error due to this cause is smaller the more efficient the filtration.

The relationship between R and N may be written

$$R = bN$$

where b is a constant.

The effect of the coloring matter on the Tyndall beam intensity may also be ascertained from Table VI. At constant turbidity the Tyndall beam intensity increases as the color decreases. When the logs of R for $U = 1$, $N = 1$ are plotted against C, a straight line is obtained. This relationship is expressed by

$$b = ak^{-C}$$

where k is a constant.

Combination of the two formulas above gives

$$R = aNk^{-C} \qquad (6)$$

This formula is similar to the one found previously for the Filter-Cel–caramel series, but it is simpler because within the range investigated R is proportional to N itself, not to log N. The values of the logs of the constants a and k in the above formula are

	Blue	Green	Red
log a	2.32117	2.79288	3.27835
log k	0.25256	0.10687	0.03982

Upon substituting these constants and the known values of C and N in formula 6, the data presented in Table VIII are obtained. These show good agreement with the experimental values of Table VII in most cases.

Transmittancy. The corrections for the residual turbidity in the two filtered sirups, shown in Tables VI and VII, were now applied to the transmittancies also, and it was found that Beer's law holds for the range studied experimentally and well within the limits of error for both color and turbidity. The relationship may be expressed by the formula

$$-\log T = mN + nC \qquad (7)$$

The values of the constants m and n are

	Blue	Green	Red
m	0.15510	0.10408	0.07461
n	0.17718	0.08669	0.03416

Upon substituting these values and those for C and N in formula 7, the transmittancies shown in Table VIII are obtained. These agree satisfactorily with experimental values shown in Table V.

Since Beer's law holds for the transmittancies in respect to both C and N, these may be expressed directly in terms of $-\log T$, as previously proposed by Balch:

$$-\log T = C + N \qquad (8)$$

In this case the constants in formula 6 assume the following values:

	Blue	Green	Red
log a	3.13056	3.77551	4.40555
log k	1.42545	1.23280	1.16568

C and N may then be calculated from formulas 6 and 8:

$$\log R = \log a + \log N - (-\log T - N) \log k$$

whence

$$N + \frac{\log N}{\log k} = \frac{\log R}{\log k} - \frac{\log a}{\log k} + (-\log T)$$

The values of N corresponding to those of $N + \log N/\log k$ must be found from specially prepared tables or graphs, and C is then found from formula 8. Or the entire solution may be found from a graph, as shown in Figure 1.

Table VIII. Calculated Tyndall Beam Intensities and Transmittencies of Mixtures Listed in Table VII

Mixtures	Tyndall Beam Intensities			Transmittancy		
	Blue	Green	Red	Blue	Green	Red
5 C units						
5 U, 0 F, 0 W	57.19	906.8	6001	2.18	11.12	28.59
4 U, 1 F, 0 W	47.44	730.1	4842	2.96	14.04	33.75
3 U, 2 F, 0 W	37.67	553.3	3681	4.01	17.74	39.85
2 U, 3 F, 0 W	27.91	376.7	2522	5.44	22.41	47.04
1 U, 4 F, 0 W	18.14	200.0	1361	7.38	28.30	55.54
0 U, 5 F, 0 W	8.38	23.21	201.6	10.01	35.75	65.56
4 C units						
4 U, 0 F, 1 W	81.99	929.7	5274	4.68	17.22	36.66
3 U, 1 F, 1 W	64.33	712.3	4020	6.36	21.56	43.19
2 U, 2 F, 1 W	46.65	495.4	2787	8.66	26.97	50.73
1 U, 3 F, 1 W	28.99	278.1	1546	11.89	33.76	59.66
0 U, 4 F, 1 W	11.32	59.84	305.2	16.05	42.31	70.15
3 C units						
3 U, 0 F, 2 W	110.3	893.9	4348	10.03	26.69	47.04
2 U, 1 F, 2 W	79.17	621.2	3041	13.58	33.27	54.99
1 U, 2 F, 2 W	48.02	348.3	1734	18.41	41.47	64.23
0 U, 3 F, 2 W	16.87	75.4	427	24.94	51.70	75.06
2 C units						
2 U, 0 F, 3 W	132.3	766.1	3197	21.50	41.35	60.36
1 U, 1 F, 3 W	72.94	402.2	1694	29.71	52.03	71.08
0 U, 2 F, 3 W	13.68	37.94	190	41.04	65.50	83.71
1 C unit						
1 U, 0 F, 4 W	117.4	499.4	1789	46.10	64.00	77.40
0 U, 1 F, 4 W	14.99	56.29	166.3	63.53	79.66	90.92
0 C unit						
0 U, 0 F, 5 W	6.91	22.34	75.93	98.83	99.14	99.32

The $-\log T$'s may finally be converted into $-\log t$'s by reducing them to the basis of 1 gram of dry substance in 1 cc. of solution and 1 cm. thickness.

Further research will have to show whether or not the relationships found for the particular raw sugar used in this investigation are applicable to color and turbidity determinations in other raw sugars. It is already known that the nature of the coloring matter varies from case to case, and this may be expected to be true for the turbidity also, especially as to particle size. Teorell (*6*) has found that the particle size of suspensions in colorless media may be determined by measuring either transmittancy or Tyndall beam intensity at several wave lengths, and it is possible that this observation may help to solve the present problem. Complete measurements with three color screens on about sixty different raw sugars have already been made, and turbidity has been determined in the same sugars by Balch's method. The data are being correlated in two different ways: First, the color and turbidity of each sugar are calculated by formulas 6 and 8, and correlation is attempted on the basis of Teorell's observations. The second method consists in a statistical analysis of the data, with the results by Balch's method as the criteria.

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Determination of Viscosity of Dilute Solutions of Cassava Flour and Other Starches

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After describing certain viscosity characteristics of some of the commonly known and widely used brands of cassava flour and other starches, various methods of testing are discussed and a new method and apparatus for preparing and testing dilute hot solutions are offered as standard for a large portion of the trade.

From the standpoint of laboratory testing the viscosity of starch is probably its most important variable characteristic. Certainly this is true among starches of the same kind. When starch solutions having the same concentration show the same viscosity, they will also with few exceptions have the same adhesive or sizing value. Furthermore, among starches of the same kind, uniformity with respect to viscosity frequently means uniformity with respect to other seemingly unrelated characteristics. Color, clarity, cleanness, resistance to fermentation, and fiber content can be suitably determined in the laboratory, but in general these characteristics have substantially less significance than viscosity. Broadly speaking, viscosity is the property which most largely distinguishes the various grades in any one kind of colloidal material. The direct determination of strength or sizing value on a laboratory scale is so complicated and difficult as frequently to give highly erroneous indications, even in the hands of experts.

Terms commonly used in the trade to describe the consistency of gelatinized starch solutions are viscosity, body, fluidity, plasticity, paste strength, and jelly strength. Viscosity, as it is commonly understood, has a meaning sufficiently correct and descriptive for all practical purposes when hot dilute solutions are referred to, and will be generally used in this article.

The testing of starch for viscosity has been considered a rather hopeless proposition. Although a number of enlightening articles (*1, 2, 5, 6*) have recently appeared, there is still much misunderstanding and lack of agreement on the subject. Each laboratory has had an individual and usually somewhat original method for testing, by which the results were reported in some arbitrary unit. This difficulty, however, has been well recognized and has caused little confusion. The real difficulties hindering the proper appreciation and common understanding of viscosity determinations have been far more obscure. Experienced laboratories have rarely been able to agree on the relative viscosities shown by a number of samples unless the differences were pronounced.

Substantial benefit should result to all if the general principles and difficulties involved in viscosity determination were more clearly understood.

In spite of general misapprehension regarding the starch viscosity test, it is becoming more generally realized that when all the conditions are known and properly controlled and the results properly interpreted, the values so obtained are as significant and as easy to duplicate as the average physical or chemical test used for industrial control.

Viscosity of Cassava Flour

The two great uses of cassava flour by industry are for glue, which usually requires a cold concentrated alkaline solution, and for sizing, which usually requires a hot dilute neutral solution.

This paper is principally concerned with the testing of dilute solutions of untreated cassava flour. The testing of concentrated alkaline solutions requires different methods and conditions and should be considered as a separate field. Frequently a starch having a relatively high viscosity in concentrated solution will show a relatively low viscosity in dilute solution. Even among dilute solutions, concentrations cannot be changed substantially without the possibility of bringing about a drastic shift in their relative viscosities.

The results recorded in Tables I and II were all obtained in a like manner by using the methods and apparatus described below. The "Parts of Water" shown in these tables is the ratio of water to one part of starch or flour (containing 12 per cent moisture), which was present at the time the first test was made. The data presented show that the viscosity of colloidal solutions produced by gelatinizing starch in water is largely dependent upon the conditions surrounding the preparation of the solutions.

Table I. Effect of Cooking on Viscosity of Cassava Flours

Test	Sample	Kind of Water	Parts of Water	Viscosity in Centipoises after Cooking 2 min.	7 min.	12 min.	15 min.	25 min.	35 min.	45 min.	55 min.	75 min.
1	A	Distilled	16.5 to 1	1980	1120	459	332	234	140	102	78	54
2	B	Distilled	16.5 to 1	166	140	127	102	78	54	54	27	27
3	C	Distilled	16.5 to 1	538	747	1220	1470	570	386	251	204	127
4	E	Distilled	16.5 to 1	870	676	580	465	371	262	224	166	78
5	F	Distilled	16.5 to 1	610	1020	1090	1160	665	...	305	...	166
6	F	Well	16.5 to 1	443	470	371	332	194	...	127	...	78
7	G	Distilled	16.5 to 1	550	482	472	305	166	...	78	...	27
8	G	Well	16.5 to 1	550	482	443	332	179	...	102	...	27
9	H	Distilled	16.5 to 1	1980	..	665	..	332	...	...	...	...
10	H	Distilled	18.5 to 1	1220	..	465	..	234	...	...	...	...
11	H	Distilled	22 to 1	371	..	270	..	127	...	...	...	...
12	H	Distilled	33 to 1	140	..	90	..	50	...	...	...	...
13	I	Distilled	16.5 to 1	1780	..	570	..	300	...	...	...	...
14	I	Distilled	33 to 1	194	..	140	..	54	...	...	...	...

Table II. Effect of Cooking on Viscosity of Commercial Starches

Test	Kind of Starch	Parts of Water[a]	Viscosity in Centipoises after Cooking 3 min.	10 min.	15 min.	20 min.	25 min.	35 min.	45 min.	55 min.	75 min.	After Standing 24 Hours in Cold Consistency	Clarity
15	Corn (Pearl)	12.5 to 1	708	747	..	...	890	635	482	340	214	Very firm jelly	Cloudy
16	Wheat	11.5 to 1	375	375	..	390	...	332	262	194	166	Firm jelly	Cloudy
17	Rice	11.5 to 1	498	260	..	243	...	204	179	140	78	Firm jelly	Cloudy
18	Potato (German)	21.5 to 1	2500	1660	1330	...	515	243	166	127	54	Liquid	Clear
19	Potato (Maine)	21.5 to 1	2400	1520	1200	...	580	247	140	127	54	Liquid	Clear
20	Sago	13.5 to 1	665	255	..	78	...	27	27	...	...	Soft jelly	Cloudy
21	Arrowroot	19.5 to 1	432	650	..	224	...	102	54	27	27	Liquid	Clear
22	Cassava	16.5 to 1	1800	810	..	...	277	194	140	54	27	Liquid	Clear

[a] Distilled water used.

Table I shows the effects of cooking on the viscosity of a number of samples of cassava flour, representing brands imported from Java and more or less regularly appearing on the market in this country and which so far as is known had not been treated in any manner for the purpose of modifying their viscosities.

Table II shows the effect of cooking on the viscosity of samples of a variety of starches consumed in large quantities by many industries, and known to the trade as first-quality raw or thick-boiling. In these tests the parts of water have been varied substantially for the different starches in order to give viscosities somewhere near the same order for each starch during a portion of the cooking period; also to give bodies of sufficient thickness to be sensitive to the cooking operation. Each starch can be diluted so that the resulting viscosity is very little affected by heat and agitation; for example, if the sago starch had been cooked with 21.5 parts of water, as was done with the potato starch, the sago solution would have shown a very low viscosity which would hardly have been affected by the cooking operation, whereas at the higher concentration used a rapid change in viscosity was shown.

Figure 1 shows graphically the results of tests 1, 2, 3, and 4 of Table I. These flours were all cooked with the same amount of water and were selected to illustrate the wide differences in viscosity frequently found among raw or unmodified cassava flours; also to show the necessity of measuring the viscosity at more than one point in the cooking operation.

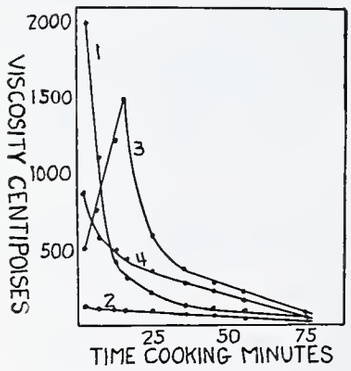

Figure 1. Effect of Cooking on Viscosity of Selected Samples of Cassava Flour

1. Sample A, 16.5 to 1
2. Sample B, 16.5 to 1
3. Sample C, 16.5 to 1
4. Sample E, 16.5 to 1

Figure 2 shows graphically the results of tests 9, 10, 11, 12, 13, and 14 of Table I. Tests 9, 10, 11, and 12 can be considered as a group illustrating the effect of dilution on the viscosity curve of cassava flour H. The nature of the viscosity curve for flour H at the lower concentrations is entirely different from that shown at the higher concentrations. Tests 13 and 14 show the same order of change for cassava flour I. Another interesting fact is shown by comparing the curves for tests 9 and 13 with 12 and 14. Test 9 is the curve for flour H at 16.5 to 1 and 13 is the curve for flour I, also at 16.5 to 1, H showing a relatively higher viscosity than I throughout. Tests 12 and 14 show the relative position of the viscosity curves for H and I at 33 to 1; the positions of these flours is reversed with respect to viscosity, sample I showing the highest viscosity for this concentration.

Figure 3 presents graphically the results of the tests in Table II. Some care must be exercised in drawing conclusions from a group of curves of this kind. The samples used for these tests are typical of the average for each starch, but it should not be assumed that all samples of any one kind of starch would conform to the type shown here. However, the curves clearly indicate that potato, cassava, sago, and arrowroot solutions are more drastically affected by heat and agitation than those of wheat, corn, and rice; also that potato solutions cover the greatest viscosity range, while wheat covers the least.

Effect of Heat and Agitation. Viscosity is usually rapidly reduced by continued application of either heat or agitation, particularly when heat and agitation are combined. Cassava flour and several other starches have a large percentage of their viscosity which is easily destroyed, provided the solutions are sufficiently concentrated, this percentage varying greatly among different brands of the same kind of starch. In general, however, those starches which show the highest initial viscosity also have the largest percentage of easily destroyed viscosity, so that when starch solutions are subjected to a prolonged period of heat and agitation the solutions of initially high viscosity are liquefied more rapidly. Flours which give solutions of initially high viscosity may after a prolonged or severe cooking period show a viscosity which does not differ substantially from that shown by the so-called low-viscosity flours, when both are subjected to the same treatment.

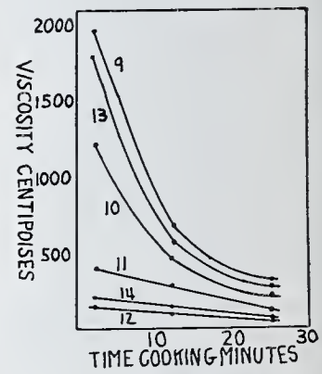

Figure 2. Effect of Concentration on Viscosity of Cassava Flour

9. Sample H, 16.5 to 1
10. Sample H, 18.5 to 1
11. Sample H, 22 to 1
12. Sample H, 33 to 1
13. Sample I, 16.5 to 1
14. Sample I, 33 to 1

All kinds of cassava flour as well as other starches develop a maximum viscosity at some point in the cooking operation, but the amount of cooking required to develop this maximum viscosity varies greatly. Curve 3, sample C, in Figure 1 shows that in order to develop the maximum viscosity for this sample, about 10 minutes' more cooking is required than for the other samples of cassava flour. This delayed development of the maximum viscosity is not frequently shown by samples of cassava flour, although other starches—corn, arrowroot, and wheat (Figure 3)—usually show this characteristic.

Two flours may develop similar maximum viscosities at the same point in the cooking cycle, but one flour may show greater resistance to the thinning action of further heat and agitation and therefore at some later point in the cooking cycle be substantially thicker than the other. (Compare curves 1 and 4, Figure 1.)

Effect of Small Chemical Changes. It is becoming fairly well recognized that the viscosity of starch solutions can be greatly affected by very small concentration of electrolytes. Ripperton (*5*) has shown the effect of some chemical additions and also that equal additions to different samples of the same variety of starch do not always produce the same relative ehange. Wiegel (*7*) states that viscosity changes were different in Thuringer glass from those in Jena glass. Attention is called to tests 5, 6, 7, and 8 of Table I. Cassava flour F was used for tests 5 and 6 and a very large reduction in the viscosity was produced by substituting first-class well water in 6 for the distilled water of 5. Cassava flour G was used for tests 7 and 8. No practical change in viscosity was produced when the well water of 8 was substituted for the distilled water of 7. These tests clearly indicate the importance of small quantities of electrolytes and show that all flours do not react in the same manner; also that gross errors might result when an attempt is made to anticipate the viscosity of pure water solutions from data obtained from chemical solutions or vice versa.

Effect of Concentration. Viscosity determinations and curves can be decidedly confusing unless the concentration is stated and the possible effect of varying the concentration is clearly understood. Significant viscosity studies and practical accurate testing have been hindered because water concentrations far below commercial requirements have been used, frequently between 30 and 100 to 1. Viscosity tests at these very low concentrations (Figure 2) are easier to make and to duplicate, but unfortunately the results so obtained lack significance. A number of samples of flour will usually show roughly similar relative viscosities at substantially different concentrations, but there are many exceptions. It is also obvious, on account of the very sensitive nature of the more viscous solutions, that the relative divergence in viscosities of flours increases with concentration.

General Methods of Testing

In recent years many methods of preparing starch solutions for viscosity determinations have been suggested. Harvey (*3*) passed live steam through a water-starch suspension and regularly drew off portions to be tested until he obtained a relatively constant value. The viscosity curve so obtained was considered an index of the viscosity of the starch and he therefore became one of the first to suggest the curve or the necessity of more than a one-point test. His apparatus and methods, however, lacked standardization and the means for delicate control. Wolff (*8*) brought starch into solution on a water bath, then boiled and stirred the mixture for 2.5 minutes. His test was apparently a one-point method and the extremely important factors of heat and agitation must have been difficult to control accurately. Ripperton (*5*), recognizing the paramount importance of the methods used to prepare solutions of starch and especially the effect of heat and agitation, devised a refined method in which he carefully controlled heat and completely eliminated agitation. His method was apparently adapted for a one-point determination and because he eliminated agitation, which actively enters into all commercial uses of gelatinized starch, appears lacking in practical value.

Grimshaw (*2*) has presented a number of methods used by different starch manufacturers, differing widely in the manner in which the solutions are prepared. In general the methods used to provide heat and agitation are meagerly described and do not offer adequate means for either control or standardization. It would seem difficult for laboratories employing any of them consistently to obtain a practical degree of agreement. Furthermore, the methods are not convenient for the determination of the viscosity curve. Caesar (*1*), with an excellent discussion of the principles involved in viscosity determinations of starch pastes, described a new apparatus and method for obtaining a complete picture of the changes which occur during the cooking and cooling periods. The method, however, does not appear suitable for

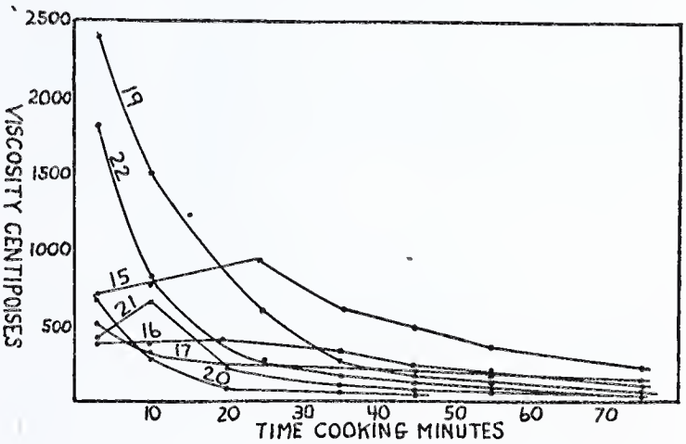

Figure 3. Effect of Cooking on Viscosity of Commercial Starches

15. Corn, 12.5 to 1
16. Wheat, 11.5 to 1
17. Rice, 11.5 to 1
19. Potato, 19.5 to 1
20. Sago, 13.5 to 1
21. Arrowroot, 19.5 to 1
22. Cassava, 16.5 to 1

ordinary control work because of its complicated nature, the length of time required to make the test, and the lack of sensitivity in the boiling range. Mangels and Bailey (*4*) in a study of the relative viscosities of wheat starches used cold solutions of chemicals as gelatinizing agents and found that different reagents showed different relationships between the starches. Obviously the values obtained by using chemical gelatinizing agents cannot be used with certainty to predict values when water and heat are used as the gelatinizing agents.

The writer has observed a number of viscosity methods used by the laboratories of the starch-consuming industries, rather than by starch manufacturers as described by Grimshaw (*2*), and has found laboratory methods also decidedly different in both principle and technic. The manner in which starch solutions were prepared for testing frequently has had no apparent relation to the manner in which the solutions were prepared for plant consumption. It has been suggested that the different requirements of the consuming industries would eliminate the possibility of adopting a standard method of viscosity determinations, but it appears that the great majority of plants using starch as a size prepare their starch by boiling it with from 10 to 20 parts of water and use it at a temperature at or near the boiling point.

The large number of methods for viscosity testing now used by the trade can be roughly divided into four general classes:

1. The starch is gelatinized in water by heat supplied from a hot water bath. The temperature employed, the time of cooking, and the agitation vary enormously. When the cooking period is comparatively short, no indication is given as to how much cooking is required to develop the maximum viscosity or what resistance the starch may have to longer cooking and agitation. When the cooking period is comparatively long, all starch solutions tend to be reduced to the same viscosity level and all indications of the body developed by a limited amount of cooking, as well as the point where the starch develops its maximum viscosity, are obscured. Accurately controlled heat and agitation seem difficult to obtain and duplicate, especially

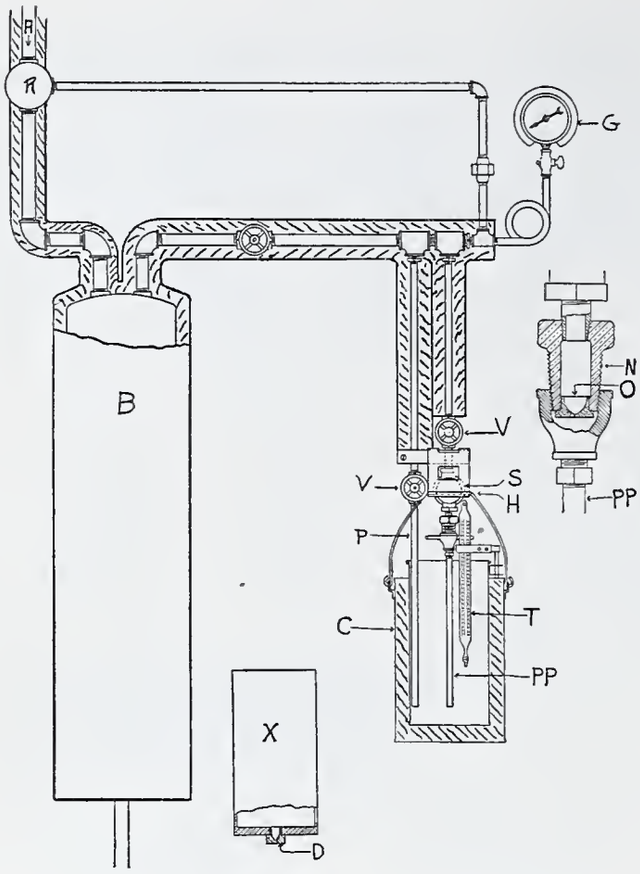

FIGURE 4. DIAGRAM OF VISCOSITY-TESTING APPARATUS

A. Steam entry
B. Water separator
C. Boiling can, copper-lined, well-insulated walls and bottom, 12 inches (30.5 cm.) deep, inside diameter 5.75 inches (14.6 cm.)
D. Viscometer orifice. Standard brass spray tip (Monarch Manufacturing Works, Inc.) Type 631, size 0.25 inch (0.635 cm.). The 0.125-inch (0.317-cm.) diameter orifice tip, weighing 8.1 grams, and the 0.22-inch (0.556-cm.) diameter orifice tip, weighing 7.1 grams, were selected as most suitable.
G. Pressure gage
N. Brass reducing plug, tapped for 0.25-inch (0.635-cm.) steam orifice
O. Steam orifice. Standard brass spray tip, Monarch type 631, 0.25 inch (0.635 cm.), with orifice hole 0.04 inch (0.102 cm.) diameter, made by No. 60 drill
P. Unrestricted steam pipe, size 0.25 inch (0.635 cm.)
PP. Orificed steam pipe, size 0.25 inch above orifice and 0.125 inch (0.317 cm.) below. Extending to depth of 1 inch (2.54 cm.) above center and bottom of boiling can
R. Pressure regulator, to maintain constant steam pressure of 25 pounds
S. Strainer, size 0.5 inch (1.27 cm.), made by Tryme Manufacturing Co., Westfield, Mass.
T. Thermometer, detachable. Mercury bulb suspended 4 inches (10.2 cm.) from bottom and 2 inches (5.1 cm.) from side of boiling can.
V. Globe valves, size, 0.25 inch (0.635 cm.)
X. Viscometer cup. Brass, outside diameter 3 inches (7.6 cm.); outside height 5.875 inches (14.9 cm.). Walls made of No. 18 Stubs gage Star Brand seamless brass tubing, bottom thickness 0.187 inch (0.47 cm.), tapped in center of bottom for insertion of 0.25-inch (0.635-cm.) orifice; weight of cup without orifice, 530 grams.

in different laboratories, when heat is applied by means of a water bath and agitation is supplied by some other means.

2. Frequently the starch is cooked for a short or long period, then allowed to cool by standing several hours. The firmness of the jelly so formed is measured either by some jelly-strength apparatus or more frequently by comparing the feel of the jelly with that of a standard sample. Starches so tested are usually used by the factory operation in a hot liquid state. Since the consistency of a cold starch solution which has stood for several hours without agitation is only very poorly related to its consistency while hot and agitated, this method quite frequently gives erroneous results. Furthermore, the consistency of a cold starch jelly is very difficult to measure or estimate accurately.

3. Starch is often gelatinized in cold or hot water by means of caustic soda, and then tested. Since dilute solutions of starch are rarely gelatinized by caustic for practical application and since such a method of gelatinization will not reliably indicate the consistency of starch during or after cooking with water alone, this method seems to have limited practical value.

4. Starch is cooked by running live steam directly into the solution. The temperature rises to near the boiling point of water and remains steadily at that point during the operation, the agitation of the solution during the cooking being controlled by the amount of steam released. This method is employed by the great majority of large starch consumers in their plant operations and for that reason has especial significance when adapted to a laboratory method for indicating the practical value of a sample of starch. So far as is known, however, this method has not been generally used with success in the laboratory because its action is rapid and requires a very definite control. The new apparatus described below makes use of this method of cooking and discloses means for accurate control.

Many different kinds of instruments are used in measuring the consistency of starch. Most of them are satisfactory for practical purposes, but some are better adapted to the testing of hot dilute solutions than others. The stationary orifice type, including the Saybolt, the Engler, the Scott, and the ordinary glass funnel, are widely used. These instruments usually require some sort of temperature control to keep solutions from cooling too much during the test. The orifice is also subject to stoppage if clots or lumps of cooled starch solution collect, and the solution to be tested must be removed from the cooking container in order to pass it through the orifice. The frictional and torsional types, such as the Störmer and the MacMichael, also require removal of the solution from the cooking container as well as temperature control to prevent cooling of the solution in the viscometer. The readings, however, are not appreciably affected by small lumps or clots.

The Bingham-Greene plastometer, where the solution is extruded through a capillary under pressure, has also been used but is best adapted to thick pastes lacking the viscous nature of hot dilute starch solutions.

Nivling has developed an automatic continuous recording viscometer for large-scale industrial uses where the pressure required to deliver a given volume of liquid at a constant rate is used as a measure of viscosity.

PROPOSED VISCOSITY TEST

Having in mind the general lack of confidence and agreement in the results of viscosity testing and the great variety of methods used, a new method was developed which it is believed provides controlled conditions which can be easily duplicated. Boiling with live steam is the method of cooking employed, because it is widely used by the plant operations of large consumers. Heat and agitation are definitely controlled by a constant flow of dry steam through a standard orifice. It has previously been shown that a sample of starch frequently has a peculiarly individual as well as a rapidly changing viscosity, so that for many purposes a single-point determination during the cooking operation has little or no practical significance. This new method, because it easily permits a continuous testing of the solution during the cooking period, is suited for the determination of the viscosity curve.

An important feature of this method is the viscometer, which is a modification of the original Perkins viscometer described in U. S. Reissue Patent 13,436. The modified viscometer is a metal cup with an orifice screwed into its bottom. The cup is simply placed in the solution to be tested and the time required for its submergence is measured by a stop watch. This viscometer eliminates many of the objectionable features of the viscometers now in common use. The solution is not removed from the cooking can during the test. No special temperature control of the viscometer or solution is necessary during the measurement, since the viscometer passes through a large quantity of solution contained in the insulated cooking can rather than a comparatively small amount of solution passing through a rather large viscometer. This viscometer is easy to make, inexpensive, practically unbreakable, and

very easy to clean. Its accuracy as well as the ease and time required for its manipulation have been highly satisfactory. It has been developed to measure the degree of thickness or thinness of dilute solutions of starch in terms having practical utility and not to determine whether the consistency is truly viscous or whether a set of readings follows some mathematical equation. A good viscometer for practical purposes should indicate only differences which are apparent to the skilled practical man.

Method of Testing. Place 3000 cc. of distilled water at about 75° F. (23.89° C.) in the boiling can and stir in the proper amount of starch. Open valve pipes *P* and *PP* to drain condensation and heat them; then close the valves, attach the boiling can to hook *H*, and open wide the valves or pipes *P* and *PP*. After 20 seconds the mixture will gelatinize and the flow of steam through *P* must be reduced immediately, so that the force of the steam will not blow the paste out of the can. Continue to manipulate the valve for *P*, so that the temperature is brought steadily up to 190° F. (87.78° C.) in exactly 1.5 minutes. Thereupon, immediately close the valve for *P* but allow the constant flow of steam through *PP* and the constant agitation caused thereby to continue as long as desired. The temperature of the solution rises rapidly to the boiling point, where it remains. It has been the custom of this laboratory when testing cassava flour for ordinary control purposes to use 200 grams and to remove the can for testing 3 minutes after opening valve pipe *P*. At this point the viscometer cup with a 0.22-inch (0.556-cm.) orifice is placed in the solution; the time required for the cup to submerge is the viscosity measure. Exactly 2 minutes after the removal of the can it is replaced and boiling is continued until the total time elapsed has reached 17 minutes, whereupon the can is again removed and tested with a 0.125-inch (0.317-cm.) orifice in the viscometer. The first reading with the 0.22-inch (0.556-cm.) orifice can be converted into equivalent readings for the 0.125-inch (0.317-cm.) orifice by means of a predetermined set of values, and these viscosity readings in seconds can be converted into centipoises after standardizing the 0.125-inch (0.317-cm.) orifice against solutions having a known viscosity in centipoises. For ordinary purposes readings in seconds are preferred.

Standardizing Apparatus. To standardize the cooking apparatus, open wide the valve for pipe *PP* and allow steam to flow until the pipe is hot; then put 4000 cc. of water at a temperature of about 70° F. (21.1° C.) into the cooking can and place it on the hook. The time required to raise the temperature from 75° to 100° F. (23.89° to 37.78° C.) should be approximately 3 minutes and 13 seconds.

The viscometer cup is standardized by measuring the time required for it to sink in water at approximately 75° F. (23.89° C.). The cup with an 0.125-inch (0.317-cm.) orifice sinks in 19.3 seconds and with the 0.22-inch (0.556-cm.) orifice the time is 7.1 seconds.

With this apparatus and method of cooking the condensation should be very close to 350 cc. after 3 minutes of cooking and 30 cc. for every additional 10 minutes when a test is made using 3000 cc. of water and 200 grams of starch. For ordinary testing the condensation after the first 3 minutes is not an important factor.

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Determination of Dielectric Constants by Means of Radio

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In connection with research work, a method of determining dielectric constants accurately with an inexpensive apparatus was desired. The heterodyne beat method was the most convenient one to use, but a source of constant radio frequency was needed to obtain good results. Broadcasting stations should serve for this purpose, as they are required by federal regulations to keep within twelve cycles of their assigned carrier frequency to guard against interference with stations operating in adjacent channels.

If the frequency of the carrier was varied by the audio frequency superimposed upon it, a composite of which is transmitted by the sending station, the radio could not be used as a source of constant oscillations. There is, however, no shift in carrier frequency but audio modulation adds what are called side bands on each side of the carrier wave and removed from it a number of cycles equal to the modulating frequency. Another oscillator coupled to a radio receiving the modulated carrier wave of the broadcasting station can be made to form an audible beat note which has a frequency equal to the difference in cycles between carrier and the oscillator. This beat note, together with a jumble of distorted music, is given out by the radio. By slowly tuning the variable oscillator the beat note can be made to become lower in frequency and the music less distorted until, at what is called zero beat, the music is undistorted and can be heard exactly as if the second oscillator were not in operation.

Having a method of setting a variable oscillator to constant frequency, the usual procedure of the heterodyne beat method for determining dielectric constants was then followed. As is known, the dielectric constant may be taken as the ratio of the capacity of a given condenser filled with the medium to be measured, divided by the capacity of the same condenser evacuated or, for most practical purposes, filled with air. By connecting the measuring condenser in parallel with a condenser previously calibrated, the capacities are added, and if the standard condenser had been set for zero beat with the broadcast station it must be detuned an amount equal to the capacity of the measuring cell again to have zero beat. Repetition of the process with air and an unknown substance in the measuring cell makes it possible to calculate the dielectric constant.

Apparatus

Figure 1 is a diagram of an ordinary variable oscillator. The measuring cell is similar to that used by Smyth and Morgan (*8*), except that the plates are insulated by beads of glass fused to stiff platinum wires which are welded to the cylindrical plates (*5*). The standard capacity is a General Radio Type 222-L condenser. The condenser system was constructed outside of the oscillator proper, and joined to it by means of the binding posts, *P*, *P'*.

A Stewart-Warner Model 102-A superheterodyne radio was used to obtain the radio frequency from the broadcasting station. The coupling between the radio set and the variable oscillator was adjusted until the error involved in detecting

zero beat was less than that in reading the scale on the standard condenser.

In order to correct for parasitic capacity, the cell was calibrated by filling it with pure, dried benzene, as is done in the ordinary procedure.

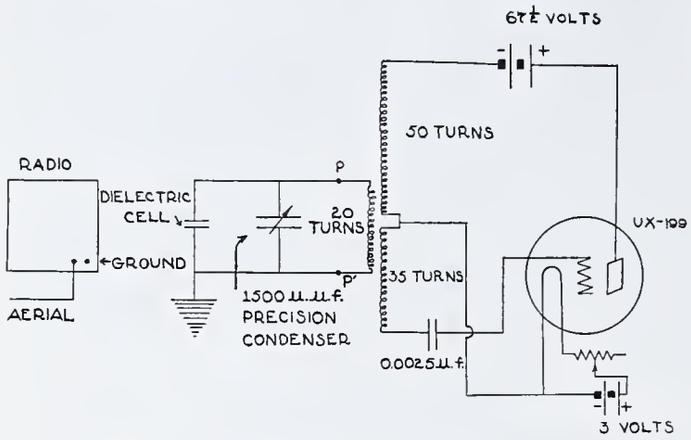

Figure 1. Diagram of Variable Oscillator

Station WGN, Chicago, operating on 720 kilocycles, was used as a source of constant frequency. Their schedule is continuous throughout the day, and the signal in this locality is of sufficient intensity for the work. Other stations may be used, and for purposes of comparison, WBBM, on 770 kilocycles, and WMAQ, on 670 kilocycles, were also used, with no variation in results. With wave lengths near the long wave limit of the broadcast band, the point of zero beat was not sharp, while with shorter wave lengths than that of WBBM, the condenser had too large capacity for the coil used.

Measurements of Dielectric Constants

In order to test the accuracy of the method, dielectric constants of some known substances were determined. The results of these measurements together with those obtained by other workers are listed in Table I. The agreement is good.

Table I. Dielectric Constants of *m*-Xylene, Carbon Tetrachloride, and Ethyl Acetate in Benzene

m-xylene

t, ° C.	ϵ Otto and Wenzke	ϵ Pyle (*7*)
36	2.349	2.353
31	2.354	2.359
28	2.360	2.365
26	2.363	2.370
20	2.369	2.374

ethyl acetate in benzene at 25° C.

Otto and Wenzke c_2	Otto and Wenzke ϵ	Smyth and Walls (*9*) c_2	Smyth and Walls (*9*) ϵ
0.04020	2.435	0.0310	2.410
0.05656	2.505	0.0475	2.477
0.1188	2.754	0.0614	2.532
0.1420	2.849	0.1060	2.708
....	...	0.1575	2.912

carbon tetrachloride

t, ° C.	ϵ Otto and Wenzke	ϵ Stranathan (*10*)
20	2.219	2.221
30	2.196	2.200
40	2.182	2.180
50	2.150	2.159

Dielectric constant data on organic compounds are obtained primarily for the purpose of calculating their electric moments. As a further check on this method dipole moments of a number of compounds were determined. The data on this work are given in Table II.

Table II. Data for Determination of Dipole Moments of Bromobenzene, *p*-Nitrotoluene, and Ethyl Bromide in Benzene at 25° C.

c_2	d	ϵ	P_{12}	P_2
bromobenzene[a]				
0.02104	0.8860	2.347	27.88	83.62
0.03134	0.8936	2.385	28.46	83.48
0.03668	0.8974	2.401	28.72	83.16
0.05633	0.9130	2.469	29.85	82.88
0.07708	0.9279	2.547	30.85	80.74
p-nitrotoluene[b]				
0.007925	0.8736	2.495	29.89	432.1
0.01086	0.8747	2.563	30.82	407.4
0.02064	0.8783	2.841	34.32	396.9
0.02094	0.8785	2.845	34.38	394.2
0.02769	0.8809	3.024	36.44	379.2
0.03984	0.8855	3.345	39.84	356.9
0.04877	0.8887	3.583	42.13	343.4
ethyl bromide[c]				
0.01084	0.8759	2.324	27.40	93.1
0.02984	0.8848	2.413	28.58	90.2
0.03604	0.8878	2.441	28.93	89.1
0.04497	0.8920	2.482	29.45	88.2
0.05804	0.8983	2.544	30.20	86.3

[a] $P_\infty = 83.9$; $P_E = 33.92$; $\mu = 1.55 \times 10^{-18}$.
[b] $P_\infty = 448$; $P_E = 37.9$; $\mu = 4.44 \times 10^{-18}$.
[c] $P_\infty = 94.2$; $P_E = 18.5$; $P_A = 11$; $\mu = 1.77 \times 10^{-18}$.

The electronic polarization of bromobenzene was obtained from the refractive index for the sodium D line, and the density of the pure liquid. That of *p*-nitrotoluene was obtained from the same measurements on solutions in benzene, and for ethyl bromide the electronic polarization was taken from the literature. Atomic polarization was neglected in the case of bromobenzene and *p*-nitrotoluene, but the value for ethyl bromide was taken from Smyth and Morgan (*8*). The values obtained—1.55×10^{-18} for bromobenzene, 4.44×10^{-18} for *p*-nitrotoluene, and 1.77×10^{-18} for ethyl bromide—compare favorably with the values in the literature, as listed in Table III.

Table III. Electric Moment Values

	Moment $\times 10^{18}$
bromobenzene	
Bergmann (*1*)	1.49
Williams (*12*)	1.50
Müller and Sack (*6*)	1.52
Das (*2*)	1.53
K. Höjendahl (*3*)	1.56
Tiganik (*11*)	1.53
p-nitrotoluene	
Tiganik (*11*)	4.44
K. Höjendahl (*3*)	4.31
Williams (*12*)	4.50
ethyl bromide	
Smyth and Morgan (*8*)	1.86
Mahanti (*4*)	1.79

The fact that the values obtained by the use of the radio are within the experimental deviations of other investigators shows clearly that this method is useful and accurate for measuring dipole moments.

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Received November 16, 1933.

Japanese Dye Production and Foreign Trade, 1933. It is conservatively estimated that the production of synthetic dyestuffs in Japan during 1933 increased by approximately 40 per cent in volume over the output during 1932. The increase in production of cotton textiles and rayon during 1933 probably increased the demand for dyestuffs by at least one-third.

Estimation of Small Amounts of Bismuth, Antimony, Tin, and Molybdenum in Copper

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A NUMBER of methods for separating small amounts of bismuth from large amounts of copper have been proposed. Those generally used depend upon separation of the bismuth as a basic salt, which may be nitrate, sulfate, chloride, or bromide in a slightly acid solution, or upon the formation of an insoluble carbonate or phosphate in ammoniacal solution. In the latter case iron is usually added to help collect the precipitated bismuth. Most of these methods work satisfactorily for comparatively large amounts of bismuth but are not sufficiently sensitive for extremely small amounts.

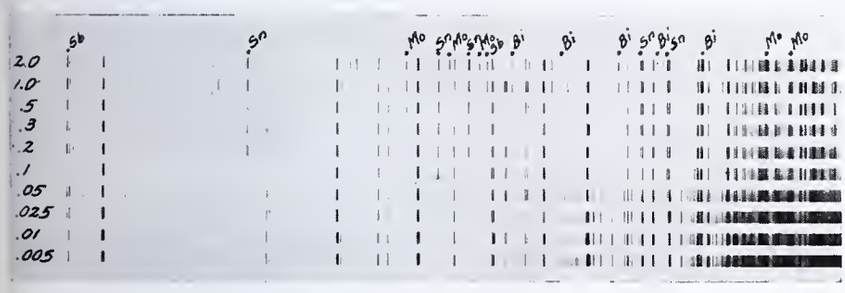

Figure 1. Spectrograms of Standard Solutions

In a previous paper (*3*) it was shown that antimony may be separated from copper by precipitating manganese dioxide in the slightly acid solution. During this work it was noticed that some bismuth accompanied the antimony and manganese dioxide, but recent experiments have shown that its precipitation is not quantitative. Bismuth was found spectrographically in each of three consecutive manganese dioxide precipitates thrown out of 1 liter of copper nitrate solution to which had been added 2 mg. of bismuth.

Moser and Maxymowicz (*1*) have shown that the precipitation of bismuth oxybromide by means of potassium bromate–potassium bromide mixtures is capable of detecting about 0.3 mg. of bismuth in 100 cc. of solution. They also have succeeded in separating 13 mg. of bismuth from about 13 grams of copper, although their error was large (13 mg. added, 20 mg. found).

By combining the precipitation as oxybromide with a simultaneous precipitation of manganese dioxide it is possible to separate less than one part of bismuth from a million parts of copper.

One hundred grams of copper were boiled with concentrated hydrochloric acid, washed with distilled water, and dissolved in 400 cc. of cencentrated nitric acid. The solution was evaporated to dryness on a steam bath, diluted with 1 liter of water, heated to boiling, and treated with 1 *N* sodium carbonate solution until a slight permanent precipitate formed. This was dissolved by the addition of 1 cc. of concentrated nitric acid. To the clear boiling solution were added 10 cc. of 20 per cent potassium bromide solution (a precipitate of silver bromide usually formed at this point), and 10 cc. of 3 per cent potassium permanganate solution. At this point manganese dioxide precipitated and bromine was liberated. The solution was boiled until free from bromine (about 30 minutes), allowed to stand until the precipitate settled out, and then filtered through a No. 4 Jena glass filter. The precipitate was washed with a little water, and the combined filtrate and washings were treated with potassium bromide and permanganate as before. After settling, the solution was filtered and the combined precipitates were dissolved with 50 cc. of hot concentrated hydrochloric acid. The pH of the filtrates varied between 2.0 and 2.6.

The hydrochloric acid solution was concentrated to about 30 cc., neutralized with ammonium hydroxide, acidified with 1 cc. of concentrated hydrochloric acid, diluted to 100 cc., heated to boiling, and treated with hydrogen sulfide until precipitation was complete. The sulfides were filtered out on a glass filter, washed with water, and dissolved with 25 cc. of hot concentrated nitric acid, followed by 10 cc. of hot concentrated hydrochloric acid. The solution of sulfides was evaporated to about 5 cc., 10 cc. of hydrochloric acid were added, and the solution was evaporated to 3 or 4 cc. It was diluted to exactly 5 cc., and portions of this concentrate were used to impregnate graphite electrodes which were dried in an oven at 100° C. and subsequently arced to give spectrograms. These spectrograms were compared with others made from solutions containing known amounts of bismuth, tin, antimony, and molybdenum, according to the procedure described by Nitchie (*2*).

Tin, antimony, and molybdenum are quantitatively precipitated along with the bismuth. This was proved in the following manner:

Three consecutive precipitations of manganese dioxide were made in a solution of 100 grams of refined copper. Practically all the antimony, tin, and bismuth were found in the first precipitate. Traces of antimony, tin, and bismuth were found in the second precipitate, but the third precipitate was spectroscopically free from all three elements. To the filtrate from the third precipitation was added 0.1 mg. of each of the four impurities, and three more consecutive precipitations were then made. The first precipitate contained all four elements. The second contained a trace of tin but no trace of the other three. The third was spectroscopically free from all four.

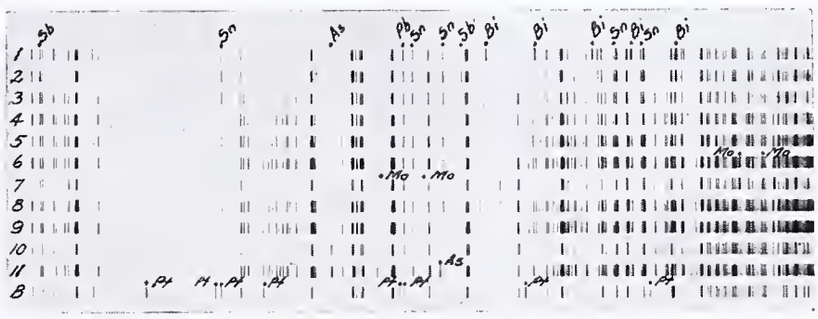

Figure 2. Spectrograms from Samples and Blank

This procedure was repeated with the addition of 2 mg. of each impurity. The results were practically the same. All the impurities were found in the first and second precipitates, but none in the third.

Silver and arsenic precipitate along with the other elements, but no experiments were performed to ascertain whether or not the precipitation is complete. A little lead also was found in the final concentrate but experiments showed that precipitation was

not quantitative. Lead was found in each of three consecutive precipitations brought down in the manner described above.

A number of samples of refined copper from various sources were analyzed, with the results shown in Table I.

Table I. Analysis of Refined Copper

Sample	Antimony	Tin	Bismuth	Molybdenum
	%	%	%	%
1	0.00013	0.00017	0.0045	None
2	0.002	0.0015	0.0005	None
3	0.0013	0.0012	0.00016	None
4	0.0004	0.00007	0.00015	None
5	0.0002	0.0003	0.00002	None
6[a]	0.00018	0.00018	< 0.00001	0.00015
7[a]	0.00017	0.00004	< 0.00001	0.0005
8	0.00005	0.00018	0.000025	None
9	None	0.00005	< 0.00001	None
10	0.00008	0.0001	< 0.00001	None
11	0.00005	0.00015	< 0.00001	None
Blank	None	0.00001	None	None

[a] An unmelted cathode deposited from a leached solution.

Figure 1 shows a number of spectrograms of the standard solutions, using 0.1 cc. for each exposure. Concentrations are given in milligrams per 5 cc. Figure 2 shows spectrograms made from the samples tested and the blank obtained by electrolyzing the filtrate from sample 9, dissolving the deposit in nitric acid, and treating as a sample. Some platinum was dissolved from the electrode in the process, as may be seen.

The section of the spectrum shown in the figures extends from about 2590 Å. on the left to 3200 Å. on the right, and includes the most persistent lines of all of the elements sought.

Acknowledgment

The author wishes to thank for their coöperation the Copper and Brass Research Association and the many copper refiners who furnished the samples.

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Determination of the Acids of Plant Tissue

III. Determination of Citric Acid

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Citric acid is oxidized to pentabromoacetone by potassium permanganate in the presence of potassium bromide. The oxidation product is extracted by petroleum ether, dehalogenated by sodium sulfide, and the bromide ion produced is titrated with silver nitrate. Quantities of citric acid of the order of 1 to 20 mg. can be determined in this manner with an accuracy of ±5 per cent. Malic acid alone of the common organic acids interferes in any way with the determination, and the error introduced by the presence of this substance is ordinarily so small as to be negligible. Inasmuch as the conversion of citric acid to pentabromoacetone is not quantitative, although in constant proportion under the conditions described, it is necessary to employ a correction factor in the calculation of the results. This factor is approximately 1.12.

Citric acid, when treated with potassium permanganate and potassium bromide under the proper conditions, is converted into the insoluble substance pentabromoacetone. This reaction was originally employed by Stahre (*6*) for the qualitative recognition of citric acid, but was placed upon a quantitative basis by the work of Kunz (*4*), and of Hartmann and Hillig (*1*); it is now widely used for the determination of citric acid in plant tissues. In order to obtain trustworthy results with the method as described by Hartmann and Hillig, it is desirable to subject at least 50 mg. of citric acid to the oxidation; furthermore, the transfer of the precipitate to the filter, and the subsequent washing and drying, require the most careful attention to details of technic.

Although of great value for many types of analytical studies, Hartmann and Hillig's method is seriously limited in usefulness for the investigation of citric acid metabolism owing to the large amount of citric acid required for accurate results. Nevertheless the specificity of the oxidation reaction upon which it is founded makes it the method of choice for the determination of citric acid. The authors have therefore sought to improve the pentabromoacetone method so that the filtration, with its attendant and necessary solubility correction, may be avoided and trustworthy results may be secured on relatively small quantities of citric acid.

It was obvious that a volumetric method to determine pentabromoacetone would be necessary. Accordingly, the authors have studied several procedures whereby this substance can be dehalogenated and the halogen determined. Kometiani (*2*) has described a method for the dehalogenation of pentabromoacetone by warm alcoholic sodium iodide in the presence of acetic acid. A careful investigation of this reaction showed that quantitative results could be obtained only under the most rigidly controlled conditions; in the authors' hands the conditions described by Kometiani invariably yielded results from 30 to 40 per cent too high. Furthermore it was observed that pentabromoacetone is unstable in ethyl alcohol solution. The reaction was not investigated in detail, but within 3 hours at least 15 per cent of the pentabromoacetone in a 0.035 per cent solution of this substance in alcohol had been converted to a product that was no longer dehalogenated by sodium iodide; after 72 hours the conversion was greater than 75 per cent. Incidentally it was noted that pentabromoacetone is unstable in ether solution also, but it appears to be stable when dissolved in chloroform or in petroleum ether.

If a freshly prepared solution of pentabromoacetone in alcohol is treated with silver nitrate, a precipitate of silver bromide separates in a few minutes at room temperature. A study of this reaction showed that it was entirely unsuited

for quantitative work: dilute (0.02 *N*) alcoholic silver nitrate liberated bromine equivalent to only 32 per cent of the substance (2 atoms = 35.25 per cent) when the solution was boiled under a reflux condenser for 45 minutes, whereas more concentrated silver nitrate solutions liberated from 60 to 70 per cent (4 atoms = 70.63 per cent) under similar conditions.

The authors have therefore turned to a reaction described by Kretov, Panchenko, and Savich (*3*), according to whom aliphatic halogen compounds are completely dehalogenated on being heated for a short time with alcoholic sodium sulfide solution. It was found that pentabromoacetone reacts quantitatively even with aqueous sodium sulfide in the cold; after acidification with sulfuric acid and removal of the hydrogen sulfide by boiling, the bromide can be conveniently determined by titration with silver nitrate in the usual way. Advantage was therefore taken of this modification of the reaction described by the Russian authors for the development of an accurate volumetric method to determine citric acid in small quantities.

Reagents

Sulfuric acid, 50 per cent: a mixture of equal volumes of concentrated acid and water.

Potassium bromide, 1.0 *M*: 11.9 grams diluted to 100 cc.

Potassium permanganate, 1.5 *N*: 47.4 grams diluted to 1000 cc.

Bromine water: saturated aqueous solution.

Ferrous sulfate: 20 grams of crystalline salt, 1 cc. of concentrated sulfuric acid diluted to 100 cc.

Sulfuric acid, 2 *N*: 28 cc. of concentrated acid diluted to 500 cc.

Petroleum ether: b. p., 35° to 50° C.

Sodium sulfide, 4 per cent: 4 grams of crystalline sodium sulfide diluted to 100 cc., prepared fresh every 2 to 3 days.

Hydrogen peroxide (halogen-free): 4 grams of sodium peroxide dissolved in 50 cc. of water with careful cooling and faintly acidified to Congo red with 50 per cent sulfuric acid (7 to 8 cc. required); prepared fresh every week.

Silver nitrate, 0.05207 *N*: 8.8462 grams of pure silver nitrate diluted to 1000 cc. 1 cc. = 2.00 mg. of citric acid or 4.714 mg. of pentabromoacetone or 4.162 mg. of bromine.

Ammonium thiocyanate, 0.05207 *N*: 3.96 grams diluted to 1000 cc. and standardized against the silver nitrate.

Ferric ammonium sulfate (ferric alum): 100 grams dissolved by warming with 100 cc. of water. Warm slightly to dissolve crystals before using.

Preparation of Solution and Oxidation of Citric Acid

The organic acids are extracted by ether from a 2-gram sample of dried and powdered tissue according to the technic described by Pucher, Vickery, and Wakeman (*5*). The procedure is designed for the determination of from 1 to 20 mg. of citric acid.

An aliquot part of the organic acid solution that will contain a suitable quantity (usually 10 cc.) is diluted with water to 25 cc., and 3 cc. of 50 per cent sulfuric acid are added. The mixture is boiled gently for a few minutes to expel traces of ether, is cooled, and 3 cc. of bromine water are added. After being allowed to stand 5 to 10 minutes, the solution is filtered with gentle suction through asbestos in a Gooch crucible into a 150-cc. beaker marked at 40 cc.; a suitable apparatus for this filtration is readily devised from a desiccator. The precipitate is washed with small quantities of water until the 40-cc. mark is reached and 2 cc. of potassium bromide are added, followed by 10 cc. of potassium permanganate. The oxidation is allowed to proceed at room temperature for 10 minutes, the solution is then chilled to 10° to 15° C. in an ice bath, and ferrous sulfate solution (20 to 30 cc. usually) is added until the manganese dioxide is dissolved.

Extraction of Pentabromoacetone

The oxidation mixture is transferred to a 125-cc. pear-shaped separatory funnel previously cleaned with chromic-sulfuric acid, and the beaker is carefully rinsed into the funnel with 25 cc. of petroleum ether, used in small portions. The funnel is shaken vigorously and the aqueous layer is drawn off. The ether is transferred to a second funnel. The aqueous solution is shaken again with 20 cc. of petroleum ether and is then discarded. The two ether extracts are combined and washed four times with 3- to 4-cc. quantities of water to remove traces of inorganic halides. A 5-cc. quantity of 4 per cent sodium sulfide is added, and the mixture is thoroughly shaken; if pentabromoacetone is present the aqueous solution becomes red, the intensity of the color being very closely proportional to the amount of citric acid originally present. (This color reaction can be used to determine from 0.05 to 1.0 mg. of citric acid photometrically; the details of the method are at present being studied.) The aqueous layer is drawn off into a 125-cc. Erlenmeyer flask, and the petroleum ether is shaken with a second 5-cc. quantity of sodium sulfide, and then three times successively with 3 to 4 cc. of water, each extract being added to the flask; 20 cc. of water, 3 cc. of 2 *N* sulfuric acid, and a few small angular quartz pebbles are added, and the solution is boiled gently for 10 minutes to expel hydrogen sulfide. It is then cooled and 1.5 *N* potassium permanganate solution is added (1 to 3 cc. usually) until a red color permanent for 15 to 20 seconds is obtained. The color is discharged by the addition of an excess of halogen-free hydrogen peroxide; 5 cc. of concentrated nitric acid and 10 cc. of standard silver nitrate are added, the solution is cooled and stirred to coagulate the silver bromide (a few drops of ether assist at this point), 2 cc. of ferric alum are added, and the solution is titrated with standard thiocyanate to a faint salmon-pink color. The end point can be duplicated to 0.02 cc. with experience. Multiplication of the number of cubic centimeters of standard silver nitrate used by the factor 2 × 1.12 gives the quantity of citric acid in the aliquot of the organic acid solution taken.

Discussion

The oxidation of citric acid to pentabromoacetone is as complete at room temperature as at 45° to 48° C., the temperature recommended by Hartmann and Hillig. A series of experiments in which the oxidation was conducted at 10°, 25°, and 45° to 48° C. gave recoveries of citric acid that varied less than 0.2 per cent. Oxidation at room temperature was therefore adopted as being more convenient.

No conditions for the oxidation could be devised in which the yield of pentabromoacetone, calculated as citric acid, was greater than 90 per cent. The reaction does, however, yield a constant proportion of pentabromoacetone under rather widely varied conditions. Hartmann and Hillig likewise noted that the yield was not quantitative and suggested that a correction factor of 1.05 be used, in addition to a weight correction for the solubility of pentabromoacetone.

The petroleum ether extraction technic described entirely eliminates this solubility correction; this is the more desirable inasmuch as the solubility of pentabromoacetone was found to be appreciably greater in solutions derived from plant extracts than in solutions obtained by oxidation of the pure acid. In eight determinations of the pentabromoacetone that remained in solution, after filtration of the crystalline product obtained essentially as described by Hartmann and Hillig, the quantity found varied from 1.1 to 2.1 mg. per 100 cc. with an average value of 1.56 mg. per 100 cc. This average is in close agreement with Hartmann and Hillig's figure of 1.7 mg. per 100 cc. Four solutions derived from the oxidation of extracts from tobacco leaf contained 2.3 to 3.3 mg. per 100 cc., the average being 2.53 mg. It must be emphasized, however, that these determinations were made on solutions obtained in the course of a routine procedure; there was no assurance that equilibrium had been attained, nor was the salt content of the solutions controlled; under these circumstances somewhat wide variations of the solubility might be expected.

The choice of solvent for the extraction of pentabromoacetone from the reaction mixture is of great importance. Ordinary ether gave fairly satisfactory results when pure citric acid was employed, and when the procedure was carried through promptly, although it was somewhat more difficult to wash this solvent free from inorganic halides. When ordinary ether was used for the extraction of oxidation mixtures obtained from tobacco leaf extracts, however, the

presence of an interfering halogen compound derived from the oxidation of malic acid was detected in the extract. Furthermore, ether solutions of pentabromoacetone are not stable on standing. The brominated oxidation product of malic acid is not extracted from the reaction mixture by petroleum ether, and pentabromoacetone is stable at room temperature in this solvent; its use is therefore essential to the success of the present method.

The removal of the pentabromoacetone from the petroleum ether by aqueous sodium sulfide and its simultaneous dehalogenation are quantitative. The average recovery of pentabromoacetone, calculated as citric acid, in eight experiments in which the equivalent of quantities of from 5 to 19 mg. of citric acid were taken was 99.2 per cent. The error in the determination of quantities as small as 1.3 mg. was not greater than ±8 per cent; the variation with the larger amounts was ±2 per cent.

The sodium sulfide extract must be acidified and freed from hydrogen sulfide before titration with silver nitrate. Nitric acid, if used for this purpose, may give rise to small losses of halogen, consequently sulfuric acid must be employed. The solution, after being boiled for 10 minutes, is usually yellow or brown in color, and silver nitrate is promptly reduced if added; the interfering impurities are, however, easily removed by oxidation with potassium permanganate. It is best to add the permanganate rapidly until a red-brown color persists after 10 to 15 seconds agitation, and then add the hydrogen peroxide until the solution becomes colorless. Some difficulty may be experienced at this point, as it is not easy to distinguish the color of the excess of permanganate. It is essential, however, that an excess be present, as otherwise the silver bromide subsequently precipitated will be contaminated with reduced silver. The solution is frequently slightly turbid owing to the presence of sulfur and, when large amounts of citric acid have been taken, may be faintly yellow.

The factor employed in the calculation of the results depends upon a series of analyses of known quantities of citric acid, both alone and in the presence of malic acid. The effect of the presence of from 25 to 30 mg. each of fumaric, maleic, succinic, pyruvic, oxalic, and tartaric acids on the recovery of from 1 to 16 mg. of citric acid was tested in separate experiments. No interference was detected. Malic acid, however, was found to exercise a small effect and was therefore given especial attention.

The quantities of pentabromoacetone found by titration after the oxidation of from 0.6 to 1.9 mg. of citric acid corresponded to 90.3 ± 4.8 per cent in six experiments. When 6.4 mg. of citric acid were taken, the recovery was 87.5 ± 1.5 per cent in eight experiments. When from 12.8 to 16 mg. were taken, the recovery was 89.0 ± 0.6 per cent in seven experiments. The average recovery over the range 0.6 to 16.0 mg. was therefore 88.9 per cent or, if the smallest quantities are not taken into consideration, 88.3 per cent. This value leads to a factor of 1.133.

Analyses of mixtures of from 3 to 16 mg. of citric acid with 30 mg. of malic acid gave an average recovery of 90.8 per cent in seven experiments; analyses of mixtures of 16 mg. of citric acid with from 6 to 12 mg. of malic acid gave a recovery of 89.1 per cent in seven experiments. The average figure of 90.0 per cent recovery may therefore be taken as the most probable value of the recovery of quantities of citric acid in the range of 3 to 16 mg. in the presence of from 6 to 30 mg. of malic acid. This leads to a factor of 1.111.

It therefore seems justifiable to take the average of these factors—namely, 1.12—as an empirical factor to employ for the calculation of the citric acid from the titration value of the pentabromoacetone derived from the oxidation of mixtures which may or may not contain malic acid. The accuracy of the results so obtained is certainly well within ±5 per cent.

Data are presented in Table I which illustrate the reproducibility of the results obtained by the present method when applied to an extract from tobacco leaf tissue. The solution analyzed represented a mixture of the organic acid fractions obtained by extraction with ether from a number of different samples, and was of such a concentration that a 10-cc. aliquot part represented 0.200 gram of the dried leaf. For purposes of comparison, analyses by the gravimetric method of Hartmann and Hillig are also shown. In column 6 are given the solubility corrections, determined by the present method in the filtrates, to be added to the weight of the pentabromoacetone found. In column 7 are the solubility corrections calculated from Hartmann and Hillig's correction factor. In the last two columns these two corrections are respectively applied to calculate the proportion of citric acid in the tissue.

Table I. Citric Acid Determined in Tobacco Leaf Tissue by the Pentabromoacetone Method

Sodium Sulfide Method			Gravimetric Method					
					Solubility correction			
Aliquot	Citric acid		Aliquot	Citric acid	Found	Calculated	Citric acid	
Cc.	*Mg.*	%	*Cc.*	*Mg.*	*Mg.*[a]	*Mg.*[b]	%[c]	%[d]
25.0	13.96	2.79	25.0	10.93	3.0	1.9	2.79	2.57
25.0	14.40	2.88	25.0	11.02	2.6	1.9	2.72	2.58
20.0	11.97	2.99	25.0	11.91	2.6	1.9	2.90	2.76
20.0	11.97	2.99	50.0	25.99	3.9	2.1	2.99	2.81
20.0	11.74	2.94	50.0	26.20	2.7	2.1	2.89	2.83
20.0	11.60	2.90						
10.0	5.68	2.84						
10.0	5.66	2.83						
10.0	5.76	2.88						
5.0	2.68	2.68						
5.0	2.70	2.70						
	Av.	2.84				Av.	2.86	2.71
		±0.15					±0.14	±0.14

[a] Determined by analysis of filtrate after filtration of the pentabromoacetone.
[b] Calculated from Hartmann and Hillig's factor of 1.7 mg. per 100 cc. of reaction fluid.
[c] From data in column 6.
[d] From data in column 7.

The results in the table have not been corrected by the factor 1.12; when this is applied the average result by the sodium sulfide method is 3.18 per cent. When Hartmann and Hillig's factor of 1.05 is applied to the data obtained by the gravimetric method, the average result is 3.00 per cent from the data in column 8, or 2.84 per cent from the data in column 9. It would therefore appear that the sodium sulfide method gives slightly higher results than the gravimetric method. The difference, however, may be more apparent than real, inasmuch as it is largely a matter of the choice of factors.

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Correction. In the paper, "Acidity Titration of Low-Grade Rosins," Ind. Eng. Chem., Anal. Ed., **6**, 122 (1934), references were not made to the work of Tingle, *J. Am. Chem. Soc.*, **40**, 873 (1918), showing results obtained with the use of a pocket spectroscope in titrating sulfuric acid solutions colored by copper sulfate and by extracts of tea and stick licorice, or to the work of Macmillan and Tingle, J. Ind. Eng. Chem., **12**, 274 (1920), on determining the acidity of red wines and fruit juices. The omission of these references was inadvertent and the writer wishes to call attention to the work of these authors. W. C. Smith

Double-Acid Method of Optical Analysis of Beet Products

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A method previously proposed has been further developed for the determination of sucrose and raffinose in beet products which cannot be analyzed accurately by any single-acid inversion method. Advantage is taken of the fact that the optically active nonsugars become inactive in strongly acid solutions, as in a Clerget inversion, by making two acid inversions and polarizing one in its neutralized solution. The polarizing effects of this ammoniacal neutralization have been established, as well as the effects of leading and deleading upon the inversion constants. Analyses of molasses from widely separated districts, comparing the results by the established single-acid inversion methods, the double-enzyme method, and the newly proposed method, show the double-acid method to be comparable to the double-enzyme inversion method, whereas the single-acid inversion methods in general use give results that are seriously in error. Analyses of synthetic sirups by the double-acid method account satisfactorily for known amounts of sucrose added to beet molasses. The effect of molasses impurities upon inversion constants is considered in a preliminary manner.

The method has been developed and used at the Johnstown molasses refinery during the past 6 years, and is now offered as a substitute for the admittedly basic but impractical double-enzyme method.

The inadequacy of methods for the determination of sucrose and raffinose in beet products has been recognized for some time. The various modifications of the Clerget inversion are known to give questionable and inaccurate results, the errors being of unknown and varying magnitudes. Various procedures have been proposed to eliminate some of the sources of error, but the beet-sugar chemist has apparently found them wanting, as is evidenced by their failure to receive general acceptance.

The double-acid method described in this paper has been found both accurate and practical.

All beet-sugar products contain optically active substances of three classifications—sucrose, raffinose, and a group of polarizing nonsugars. In addition, small quantities of invert sugar, usually of negligible influence on the polarizations, are sometimes present. It is then self-evident that any single inversion method giving only two polarizations, the direct and inverted, and therefore only two equations, is inadequate. The beet chemist almost universally ignores the polarizing value of these nonsugars and therefore seldom, if ever, obtains accurate results. It will be shown that the magnitude of these errors is such that they cannot be rightfully ignored.

Another fault in the generally accepted methods is the use of various clarifiers or decolorizing agents in the inverted polarization. Even the best of these introduce no small discrepancies in the final results.

Appreciating the importance of the errors involved in the current single-acid inversion methods, Paine and Balch developed the double-enzyme method (*1*, *9*, *10*) which permits the evaluation of the three unknowns. This is admittedly the most basic and accurate method yet devised. Though this enzyme method filled a long recognized need in beet-sugar chemistry, it has not been accepted for general use because, if properly conducted, the enzyme inversions require more time than is usually available and the cost is prohibitive. The cost of the purchased enzymes used in the work reported in this paper was about $1 per determination and it is doubtful that enzymes of as satisfactory quality can be prepared more cheaply. Anyone who has worked with enzymes is also familiar with the difficulty occasionally experienced of securing satisfactory enzyme preparations and of being sure of the completeness of the melibiase inversions.

What the beet-sugar chemist needs is a method that will give the actual sucrose and raffinose in a product at no great expenditure of time or money. The method offered here was developed with these thoughts in mind.

Theory of Double-Acid Method

It has often been noted that the polarizing effect of the optically active nonsugars becomes zero in a strongly acid solution, such as the 0.634 N hydrochloric acid of a Clerget inversion. This has been observed in the Research Laboratory of the Great Western Sugar Company, and has also been confirmed by Paine and Balch (*9*) and by Zerban (*15*). This does not necessarily hold true for raw beet juice, but has frequently been demonstrated to hold in all beet-factory products following carbonation, and it is with such products that the beet-sugar chemist is generally concerned when determining true sugar or raffinose. For the present the chemist should confine himself to the double-enzyme method with cossettes or diffusion juice, but further work as to the adaptability of this new method to these materials is anticipated. As offered here, the new method is developed primarily for the accurate analysis of molasses, raw massecuite, and all other products following carbonation.

If it is tentatively accepted that the optical activity of the nonsugars becomes zero in a strongly acid solution and is restored upon neutralizing, it is possible to determine the polarizing effect of these substances. This can be done by making two acid inversions, polarizing the one in the acid and the other in its neutralized solution. The nonsugar effect is zero in the acid polarization, but has its full normal value in the neutralized solution. The difference between these two invert polarizations will then be the polarization of the nonsugars, after correcting for the effect involved in the neutralization itself. Hereafter the polarizing effect of these nonsugars, designated in a previous paper (*16*) as Z, will be termed the N value. The direct polarization may then be corrected for this contained N value, leaving only two unknowns, sucrose and raffinose, which can be calculated from the two equations. This is the basic principle of the double-acid method.

This method requires very little more time or expense than the single-acid inversion methods now in general use, and the results obtained are comparable to those by the double-

Table I. Analyses of Molasses, Comparing Double-Acid and Double-Enzyme Methods

No.	Source	Steffen or Non-Steffen	Campaign	Sucrose Double acid	Sucrose Double enzyme	Raffinose Double acid	Raffinose Double enzyme	N Value Double acid	N Value Double enzyme
				%	%	%	%		
1	Gering, Nebr.	S	1932–33	45.54	45.82	3.68	3.61	−1.78	−1.84
2	Gering, Nebr.	S	1932–33	48.68	48.70	3.93	4.02	−1.96	−2.15
3	Scottsbluff, Nebr.	S	1932–33	49.12	49.32	3.03	3.06	−1.61	−1.87
4	Lyman, Nebr.	NS	1932–33	50.96	50.98	1.25	1.42	−1.54	−1.89
5	Bayard, Nebr.	NS	1932–33	49.63	49.56	1.38	1.47	−1.74	−1.83
6	Minatare, Nebr.	S	1932–33	47.44	47.31	2.65	2.87	−1.46	−1.72
7	Gering, Nebr.	S	1932–33	48.95	49.02	3.49	3.43	−2.07	−2.04
8	Mitchell, Nebr.	NS	1932–33	48.49	48.52	1.30	1.29	−1.69	−1.72
9	Gering, Nebr.	S	1932–33	48.10	48.38	4.18	4.09	−1.99	−2.10
10	Lyman, Nebr.	NS	1932–33	51.30	51.48	1.20	1.25	−1.56	−1.84
11	Greeley, Colo.	NS	1932–33	52.64	52.61	1.17	1.31	−1.61	−1.84
12	Windsor, Colo.	NS	1932–33	48.80	48.59	0.81	0.90	−1.62	−1.58
13	Longmont, Colo.	S	1932–33	48.52	48.46	2.71	3.03	−1.52	−2.05
14	Sterling, Colo.	S	1932–33	48.41	48.43	2.76	2.89	−1.59	−1.86
15	Johnstown, Colo.	S	1932–33	47.00	46.82	3.11	3.22	−1.10	−1.12
16	Grand Jct., Colo.	S	.....	48.31	48.30	3.20	3.26	−1.12	−1.32
17	Windsor, Colo.	NS	1929–30	47.02	46.91	1.52	1.70	−1.42	−1.61
18	Fort Collins, Colo.	S	1929–30	48.90	49.07	3.57	3.43	−1.65	−1.57
19	Windsor, Colo.	NS	1929–30	47.92	47.71	1.54	1.55	−1.69	−1.50
20	Fort Collins, Colo.	S	1929–30	47.40	47.34	3.56	3.35	−1.96	−1.50
21	Billings, Mont.	S	1932–33	48.74	48.81	3.49	3.43	−1.18	−1.13
22	Lovell, Wyo.	NS	1932–33	49.48	49.38	1.57	1.75	−1.17	−1.41
23	Worland, Wyo.	S	1932–33	49.38	49.43	3.59	3.57	−1.23	−1.26
24	Paul, Idaho	S	1932–33	49.14	49.04	3.45	3.44	−1.49	−1.40
25	Idaho Falls, Idaho	S	1931–32	50.00	50.02	3.27	3.24	−1.28	−1.25
26	Garland, Utah	S	1931–32	49.74	49.52	2.94	3.10	−1.25	−1.42
27	Mt. Pleasant, Mich.	NS	1932–33	50.71	50.75	1.21	1.30	−2.95	−3.14
28	Caro, Mich.	S	1932–33	47.67	47.38	2.72	2.87	−2.00	−1.98
	Averages			48.86	48 85	2.58	2.64	−1.62	−1.71
	Differences			0.01		0.06		0.09	

enzyme method, in almost all instances. As Lundell (*7*) has recently suggested, it is well to mention at this time the cases where the proposed method will not work.

If a molasses contains a large percentage of invert sugar or its decomposition products, dependable analyses cannot be obtained by the double-acid method. Examples of this will be shown later where California beet molasses were analyzed. However, the failure of the proposed procedure on such materials holds true also with any acid inversion method. The chemist must in this case resort to the double-enzyme inversions if definitely accurate results are desired, but the double-acid method will give more accurate results on such materials than will any of the single-acid methods in present use.

When first presented (*16*), the double-acid method was in more or less of an empirical stage, but during the past year considerable work has been done on the factors and constants involved, and the method has been applied to the analysis of a large variety of molasses and synthetic products with satisfactory results.

In the analyses reported herein, carefully standardized apparatus was used. The polariscope used was a Bausch and Lomb, double-field, single quartz wedge compensating, Bates and Jackson scale type. The polarizations reported are the averages of no less than ten observations after being corrected to Bureau of Standards tested quartz plates of the same or nearly the same optical value.

Experimental Applications

The logical procedure for testing the accuracy of this double-acid method in a practical way was to apply it to the analysis of a variety of actual samples of known composition. The most severe test of any such method is with molasses in which the impurities, raffinose and optically active nonsugars, are concentrated to the highest degree. A large number of beet-molasses samples from widely separated districts covering the entire sugar-producing area of the United States were gathered for this purpose. Samples were obtained from many of the beet-sugar companies representing both Steffen and non-Steffen process houses, mostly from the 1932–33 campaign, but a few of earlier production. Such a variety should be representative of different beet-growing conditions and areas, as well as operating conditions.

All these samples were analyzed by the double-enzyme and double-acid methods. In the enzyme method the official A. O. A. C. procedure (*1*) was followed, with a few modifications. The enzyme inversions were made at room temperature and were allowed to stand for 24 hours to insure complete inversion. They were then made to volume, were covered with a few drops of toluene, and were left another 24 hours to eliminate mutarotation.

In both methods the original solution was made up at 1.0 N concentration (26 grams of molasses per 100 ml.), and the invert readings were made at 0.5 N concentration in a 400-mm. jacketed tube. Before completing the leaded solution to volume, it was well deaërated under vacuum; experience has shown that the neglect of this precaution may in extreme cases cause an error of as much as 0.2° in the direct polarization of a molasses containing much entrained air. From the final values of both methods a deduction of 1.0 per cent was made to allow for the volume of the lead precipitates. This deduction, whether made or not, obviously affects both methods alike.

The acid inversions were made by the Walker procedure (*14*), slightly modified. The Browne and Gamble (*4*) inversion constants of −33.00 and 0.514 for sucrose and raffinose, respectively, were used in the calculation of the double-acid analyses. The negative constituent of the divisor was corrected in each case by the formula: $-(32.1 + 0.07\,g)$ where g is the grams of sucrose taken for the inversion. Some claim that the negative constituent varies with the total sugar or dry substance concentration in accordance with Vosburgh's rule (*13*) rather than with the sucrose concentration. However, since the official double-enzyme method (*1*), as used here, corrects the divisor on a sucrose basis, the divisors in the acid analyses were also based on sucrose to permit true comparisons. The neutralization correction in the double-acid analyses was obtained as later described.

The results by enzyme analysis were taken as the basic or true compositions of the various samples. The percentages of sucrose, raffinose, and the N values found by the two methods are shown in Table I.

In comparison with the enzyme values, the results in Table I leave little to be desired as to the dependability of the double-acid procedure. If Lundell's apt and logical suggestions (*7*) were followed, all such results would be recorded to only one decimal and the differences on individual samples would appear even smaller. However, even considering the unreasonable second decimal, the two methods check very closely, certainly well within analytical error limits.

The average raffinose by the two methods agrees within

less than 0.1. Previously (*16*) it was found necessary to apply a correction factor of 1.18 to the raffinose percentage found by double-acid inversion. The explanation of this discrepancy is uncertain but it is possible that in the former work proper consideration was not given mutarotation in either the acid or enzyme analyses. Slight changes and improvements have also been made in the general procedure of the new method. At any rate the double-acid method is now shown to give accurate raffinose values without the application of any arbitrary correction factor.

That the basic premise of this double-acid method is sound, is shown by the agreement between the *N* values determined by the double-acid and double-enzyme methods in Table I, the average difference again being less than one-tenth. The range of *N* values by both methods is about −1.0° to −2.0° (in one case, sample 27, −3.0°). In this connection it is interesting to compare the values of Kindt (*6*), who found, after complete fermentation of the sugars in molasses, residual *N* values of a range of −1.6° to −2.7°.

The double-acid, as well as any single-acid inversion, is not dependable when applied to a product containing an unusually high percentage of invert sugar or its decomposition products. This probably explains the fact that the double-acid and double-enzyme analyses of six California molasses do not check each other, as shown in Table II. It has not been definitely proved, however, whether the discrepancies are entirely due to this cause or whether the behavior of the optically active nonsugars in these molasses is partly responsible. These samples contained considerable invert sugar and were of such low pH that the presence of appreciable quantities of decomposition products was apparent. Even though the double-acid results on such materials are not very comparable to those by enzymes, they are more so than are the single-acid inversions. Any acid inversion method will not even approximate the true raffinose percentage in such materials if the enzyme figures are accepted as correct. Evidently, the chemist working with such products has a problem peculiarly his own and must resort to enzyme inversions if the true compositions of his materials are required.

Too much attention must not be given the *N* values in Table II because, as determined by enzymes, they are too high. Invert sugar, and probably its decomposition products, cause the *N* value as calculated from enzyme inversions to be falsely large.

In Table III are shown the sucrose percentages in fifteen molasses samples as determined by three modifications of the commonly used single-acid methods compared to the double-acid and the basic double-enzyme results. The beet-sugar chemist has generally been reporting the sucrose in molasses from 1 to 3 per cent too low, as the result of the inadequacy of the methods used. In fact, when these results are expressed in terms of true purity, his results have been as much as 4.3 points too low and seldom within 1 point of the true value. Such discrepancies are too great to be continually ignored, either by the chemist or by the industry as a whole.

Unfortunately the methods now in common use do not give results that are low by any consistent amount. As shown in Table III, a result may be within 0.1 of the truth with one molasses, yet on another low by over 3.0 points. To make the case against the methods now in general use even more serious, they are not low by any consistent value at a given factory during one campaign. It has been found that the true purity of molasses was reported from 0.77 to 2.62 low at one factory during the past campaign and from 0.98 to 3.10 low at another. As a result of these errors it is difficult, if possible at all, to compare operating results from one time to another. This very likely explains why extraction does not always coincide with reported changes in molasses purities.

Though the predominating cause of the errors in the single-acid inversion methods lies in ignoring the *N* value, the reagents used for decolorizing the inversions cause appreciable and variable errors. The double-acid method inverts the same leaded and deleaded solution that is used for the direct polarization, as is the case with the enzyme inversion. However, even if the single-acid inversions were also commonly made on the leaded and deleaded solution, the results would be low by very inconsistent amounts, due to the variations in the *N* values. As shown in Table I, the *N* value varies in molasses from different districts from −1.12 to −3.14 and even greater variations have been found. Again, this *N* value is not consistent for a given factory or district. During one campaign at one factory the polarizing effect of these nonsugars varied from −1.17 to −2.67 and at another from −0.87 to −2.37° S.

Table II. Analyses of California Molasses

(Double-acid, double-enzyme, and single-acid inversion)

No.	Source	Steffen or Non-Steffen	Campaign	Sucrose: Double acid	Sucrose: Double enzyme	Sucrose: Single acid	Raffinose: Double acid	Raffinose: Double enzyme	Raffinose: Single acid	*N* Value: Double acid	*N* Value: Double enzyme	pH	Invert Sugar on Dry Substance
				%	%	%	%	%	%				
29	Santa Ana	S	1932	47.62	46.48	47.16	−0.37	0.61	−0.51	−1.55	−2.24	6.0	2.93
30	Alvarado	NS	1932	50.19	49.49	47.54	−0.51	0.30	−0.29	−2.09	−2.85	6.9	0.61
31	Oxnard	S	1932	48.53	48.39	45.72	0.39	1.10	1.36	−1.96	−3.15	6.9	1.20
32	Santa Ana	S	1933	53.77	51.49	48.24	−0.55	0.84	1.14	−2.13	−2.46	7.1	1.88
33	Alvarado	NS	1933	51.94	51.12	49.90	−0.08	0.56	−0.08	−2.04	−2.44	7.6	0.68
34	Tracy	S	1933	52.42	52.18	...	0.50	0.84	....	−1.62	−1.98	7.0	0.64

Table III. Per Cent Sucrose in Molasses

(Double-acid, single-acid, and double-enzyme methods)

Sample	Double Acid: Sucrose	Double Acid: Difference[a]	Single Acid: Darco Carbon[b] Sucrose	Darco Carbon[b] Difference[a]	Hydrosulfite[b] Sucrose	Hydrosulfite[b] Difference[a]	Zinc[b] Sucrose	Zinc[b] Difference[a]	Double Enzyme Sucrose
2	48.68	−0.02	45.26	−3.44	...	....	...	....	48.70
3	49.12	−0.20	46.40	−2.92	...	....	...	....	49.32
4	50.96	−0.02	49.67	−1.31	50.63	−0.35	50.80	−0.18	50.98
5	49.63	0.07	47.84	−1.72	48.85	−0.71	48.91	−0.65	49.56
6	47.44	0.13	45.10	−2.21	45.81	−1.50	45.86	−1.45	47.31
7	48.95	−0.01	45.76	−3.20	46.99	−1.97	47.12	−1.84	48.96
8	48.49	−0.03	46.95	−1.57	...	....	47.92	−0.60	48.52
9	48.10	−0.28	45.02	−3.36	46.30	−2.08	...	....	48.38
10	51.30	−0.18	50.50	−0.98	51.46	−0.02	...	....	51.48
11	52.64	0.03	51.20	−1.41	51.88	−0.73	52.29	−0.32	52.61
12	48.80	0.21	46.89	−1.70	47.60	−0.99	47.82	−0.77	48.59
13	48.52	0.06	46.06	−2.40	47.26	−1.20	47.14	−1.32	48.46
14	48.41	−0.02	45.90	−2.53	46.63	−1.80	46.80	−1.63	48.43
21	48.74	−0.07	46.46	−2.35	47.47	−1.34	47.64	−1.17	48.81
22	49.48	0.10	46.85	−2.53	...	....	47.94	−1.44	49.38

[a] Difference from the enzyme results.
[b] Decolorizers used on the inversions. Sample numbers agree with those in Table I.

The results in Table III strongly indicate the need of a change in methods by the beet-sugar chemist, and the same results, along with those of Table I, show the superiority of the double-acid method over those in common use.

Analysis of Synthetic Mixtures

One of the prime requisites of a method is that it will truthfully tell how much sugar has been crystallized out and removed when a sirup of a given high purity has been reduced to a molasses of definite purity. The simplest way to test a method for this purpose is to reverse this condition by adding a known amount of sucrose to a given amount of molasses and then to analyze the molasses and the resulting synthetic sirup of enriched purity. This was done with three different molasses and the sucrose was determined by the double-acid method. As a matter of interest the enzyme analyses were also determined on two of these samples. The percentages of sucrose, raffinose, and N values found by analysis as compared to the actual compositions, calculated from the original molasses and sugar added, are given in Table IV.

Table IV. Sugar Addition Tests

Method	Experiment 1 Double acid	Experiment 1 Double enzyme	Experiment 2 Double acid	Experiment 2 Double enzyme	Experiment 3 Double acid
Original molasses, per cent sucrose	48.76	48.84	49.82	49.84	47.58
Original molasses, per cent raffinose	1.29	1.26	1.10	1.26	3.00
Original molasses, N value	−1.66	−1.74	−1.40	−1.70	−1.32
Mixture, grams molasses	30.000	30.000	30.000	30.000	30.000
Mixture, grams sucrose	100.048	100.048	100.075	100.075	99.990
Per cent sucrose found	88.14	88.17	88.44	88.44	87.83
Per cent sucrose calculated	88.18	88.20	88.43	88.43	87.90
Difference	−0.04	−0.03	−0.01	−0.01	−0.07
Per cent raffinose found	0.39	0.30	0.37	0.32	0.77
Per cent raffinose calculated	0.30	0.29	0.25	0.29	0.69
Difference	0.09	0.01	0.12	0.03	0.08
N value found	−0.42	−0.18	−0.34	−0.24	−0.35
N value calculated	−0.38	−0.40	−0.32	−0.39	−0.30
Difference	−0.04	0.22	−0.02	0.15	−0.05

At first it was planned to purify the sucrose used in these sugar addition tests, but a highly refined AA sugar from a west coast refinery was obtained of such quality that it was deemed unnecessary. This sugar gave an ash of only 0.003 per cent by incineration and had a specific conductance of 0.26 which corresponds to about 0.001 per cent soluble ash. The invert sugar content was found to be less than 0.003 per cent as determined by Schoorl's method using Luff's solution (*11*, *12*). The sugar polarized 100.0 when tested against a Bureau of Standards quartz plate of 100.75° S. This sugar was therefore used as sucrose in this and all following work, after making the proper corrections for the small amount of contained moisture.

The results in Table IV show the double acid to be thoroughly dependable from one purity to another because the quantity of sugar added to, or removed from, a sirup can be accurately determined by its use. The original molasses used in these tests were of about 60 purity and the enriched molasses, or synthetic sirups, were of about 93 purity, a range in purities which covers those usually encountered in actual practice.

The double-acid method also permits the accurate determination of raffinose and N value as well as sucrose, upon diluting these substances with a large amount of sugar. Table IV indicates that under such a test the double-acid method is as reliable a procedure as the double-enzyme inversion.

Agreement of Different Analysts

Experience has shown that different analysts, working independently, can check their own and one another's results within satisfactory limits by the double-acid method. Table V indicates just as satisfactory an agreement by the double-acid as by the double-enzyme method.

Table V. Check Analyses by Two Analysts, Per Cent Sucrose in Molasses

Sample	Double Acid Jones	Double Acid Kingsley	Double Acid Difference	Double Enzyme Jones	Double Enzyme Kingsley	Double Enzyme Difference
1	45.54	45.53	0.01	45.84	45.79	0.05
2	48.70	48.67	0.03	48.73	48.66	0.07
3	49.13	49.10	0.03	49.26	49.37	0.11
4	51.04	50.89	0.15	50.94	51.01	0.07
9	48.06	48.14	0.08	48.36	48.40	0.04
10	51.28	51.32	0.04	51.58	51.37	0.21
11	52.66	52.63	0.03	52.56	52.66	0.10
15	47.00	46.99	0.01	46.81	46.82	0.01
16	48.14	48.47	0.33	48.15	48.44	0.29
21	48.73	48.75	0.02	48.74	48.88	0.14
23	48.41	49.34	0.07	49.49	49.37	0.12
24	49.35	48.94	0.41	49.20	48.87	0.33
25	50.04	49.95	0.09	49.98	50.05	0.07
26	49.76	49.72	0.04	49.58	49.46	0.12
27	50.76	50.65	0.11	50.79	50.71	0.08
28	47.65	47.64	0.01	47.20	47.56	0.36

For further information two molasses samples were sent to each of nineteen laboratories and were analyzed by the double-acid procedure. Although few of the chemists had had any experience with the new method, the results showed a very satisfactory agreement.

Neutralization Correction

The double-acid method requires the neutralization of one of the acid inversions before polarization, and the effect of the neutralization on the rotation of invert sugar has to be established and taken into consideration. Jackson and Gillis (*5*) have shown the advantages of neutralizing the hydrochloric acid with ammonia rather than sodium hydroxide. They also determined the effect of neutralizing an acid inverted solution, containing 10 ml. of 6.34 N hydrochloric acid, with 10 ml. of 6.34 N ammonium hydroxide.

While Jackson and Gillis employed a constant sucrose concentration, Brown (*2*) afterwards pointed out that the effect of salts on polarization could be expressed in a general formula in which the effect is made proportional to both sucrose and salt concentration. On this basis the Jackson and Gillis values indicate that in the neutralized inversion the presence of the ammonium chloride and the absence of the hydrochloric acid should increase the numerical value of the acid polarization by $0.0066\,S$, where S is the percentage sucrose concentration. When first offered, this method used a neutralization correction of 0.33 for molasses of 50 per cent average sucrose concentration.

Jackson and Gillis did their work on pure aqueous solutions of sucrose, but in the double-acid method the inversions and neutralizations are made upon solutions that have been previously leaded with basic lead acetate and deleaded with ammonium dihydrogen phosphate. It seemed reasonable that the presence of the resulting ammonium acetate and acetic acid would have some effect upon this neutralization correction.

To establish the neutralization effect at various sucrose concentrations, with different amounts of basic lead acetate (55° Brix) followed by deleading with ammonium phosphate, three curves were determined as shown in Figure 1.

A represents the neutralization effect, as sugar degrees, at different sucrose concentration when 20 ml. of lead acetate were added to each 100 ml. of a solution, 50 ml. of which were used for inversion after deleading. This is the amount of lead reagent ordinarily used in the analysis of molasses. The resulting straight-line curve gives the neutralization correction as 0.0081 S.

B is plotted from the results found at various sucrose concentrations when no lead acetate was used. The correction under these conditions is 0.0047 S. Although this does not coincide with the value of 0.0066 S calculated from Jackson and Gillis' data, it represents the necessary correction as found by the authors when the neutralization is made under the specified conditions.

It is evident from Figure 1 that the ammonium acetate and acetic acid resulting from leading and deleading increase the polarizing value of the neutralization correction. At 100 sucrose concentration, 20 ml. of lead increase the correction by 0.34° S, or the difference between 0.47 and 0.81. This difference decreases as the sucrose concentration approaches zero, at which point the correction becomes zero regardless of the amount of lead used.

C was determined and plotted with the use of 4.6 ml. of lead acetate per 100 ml., to prove the neutralization correction to be proportional to the lead acetate used at any given concentration of sucrose. This rather odd amount of lead was used because it was that used in the enriched molasses sirups of about 88 per cent sugar given in Table IV.

In all the experiments plotted in Figure 1, the neutralizations were made by slowly adding 6.34 *N* ammonium hydroxide to the cooled acid invert with methyl red as the internal indicator. The solution was whirled while adding the ammonia, to avoid destruction of invert sugar by localized concentration of the ammonia. In all tests exactly 1 ml. of excess ammonia was added. This is specified to assure polarization of the neutralized invert in alkaline solution in which the nonsugars have their full optical value. This excess has been found not to change the polarization by any determinable amount.

Figure 1 shows this neutralization correction to be proportional to the two variables, sucrose concentration and milliliters of lead acetate used. From *A* and *B* the correction for 5 per cent sucrose concentration intervals and 2 ml. lead acetate intervals were calculated, as given in Table VI. *C*, determined experimentally, coincides with such a line calculated from the differences between *A* and *B*.

Raffinose concentration apparently has little, if any, effect upon this neutralization correction. A solution containing 17 per cent raffinose gave a neutralization effect of only 0.08° S when 20 ml. of lead acetate were used and a 32 per cent solution gave a correction of only 0.12° S. Mixtures of sucrose with as much as 20 per cent raffinose were found to give neutralization corrections within less than 0.10° S of that for the sucrose alone. Therefore in the practical applications of this method it is necessary to consider only the sucrose concentration when using Table VI.

It is somewhat inconvenient to estimate the sucrose concentration for the factors from which sucrose is to be calculated. For all general purposes no appreciable error will be introduced into the calculation if the direct polarization *P* is used instead of *S*, when taking the neutralization correction from Table VI. *P* is generally greater than *S* on account of the raffinose present, but unless the raffinose percentage is much greater than is generally encountered, the difference is negligible when applying the neutralization correction.

While the neutralization correction has been worked out in considerable detail to cover all conditions, it may be simplified for practical purposes by using a constant value for any particular product. Thus, for molasses clarified with 20 ml. of lead subacetate per 26 grams, the value of 0.40 may be

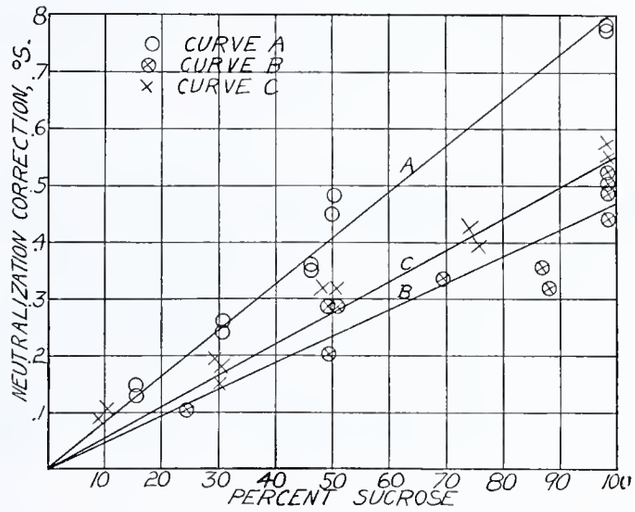

Figure 1. Neutralization Correction

used, which corresponds to 49 per cent sucrose and will not vary essentially within the ordinary range of sucrose percentage in molasses.

Inversion Constants

The method of inversion used in all this work was that suggested by Walker (*14*), slightly modified. Walker proposed heating the solution to 65° C., then adding the hydrochloric acid, and allowing to cool spontaneously for at least 15 minutes. However, in the latter part of his paper he suggests heating to 67° C. With low-grade products, such as beet molasses, a little difficulty has been found in obtaining complete inversion when the solution is heated to only 65° C., and for this reason the solutions in this method are heated to 68° to 69° C. Upon adding the 10 ml. of hydrochloric acid (d_4^{20} 1.029) the temperature at the start of inversion was found to be 64° C., dropping at the rate of about 1° per minute to 53° C. at the end of 15 minutes. This temperature is therefore somewhat comparable to that suggested by Jackson and Gillis (*5*). This modification of Walker's procedure was used in preference to that of Jackson and Gillis, because

Table VI. Neutralization Correction

Concentration[a] Per Cent Sucrose	Lead Subacetate (55° Brix)										
	0	2	4	6	8	10	12	14	16	18	20
	Ml./100 ml.										
5	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04
10	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.07	0.08	0.08
15	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.11	0.12	0.12
20	0.09	0.10	0.11	0.11	0.12	0.13	0.13	0.14	0.15	0.16	0.16
25	0.12	0.13	0.13	0.14	0.15	0.16	0.17	0.18	0.19	0.19	0.20
30	0.14	0.15	0.16	0.17	0.18	0.19	0.20	0.21	0.22	0.23	0.24
35	0.16	0.18	0.19	0.20	0.21	0.22	0.24	0.25	0.26	0.27	0.28
40	0.19	0.20	0.22	0.23	0.24	0.26	0.27	0.28	0.30	0.31	0.32
45	0.21	0.23	0.24	0.26	0.27	0.29	0.30	0.32	0.33	0.35	0.36
50	0.24	0.25	0.27	0.29	0.30	0.32	0.34	0.35	0.37	0.39	0.41
55	0.26	0.28	0.30	0.31	0.33	0.35	0.37	0.39	0.41	0.43	0.45
60	0.28	0.30	0.32	0.34	0.36	0.38	0.40	0.42	0.45	0.47	0.49
65	0.31	0.33	0.35	0.37	0.39	0.42	0.44	0.46	0.48	0.50	0.53
70	0.33	0.35	0.38	0.40	0.42	0.45	0.47	0.50	0.52	0.54	0.57
75	0.35	0.38	0.40	0.43	0.45	0.48	0.51	0.53	0.56	0.58	0.61
80	0.38	0.40	0.43	0.46	0.48	0.51	0.54	0.57	0.59	0.62	0.65
85	0.40	0.43	0.46	0.49	0.52	0.54	0.57	0.60	0.63	0.66	0.69
90	0.42	0.45	0.48	0.51	0.55	0.58	0.61	0.64	0.67	0.70	0.73
95	0.45	0.48	0.51	0.54	0.58	0.61	0.64	0.67	0.70	0.74	0.77
100	0.47	0.50	0.54	0.57	0.61	0.64	0.67	0.71	0.74	0.78	0.81

[a] Direct polarization *P* may be used instead of per cent sucrose.

it is more convenient for a large number of determinations at one time and the manipulation is somewhat more foolproof.

The inversions were all allowed to stand 2 hours before cooling and making to volume. Two hours were taken to assure complete inversion and allow as much time for the destruction of mutarotation as would generally be permissible in actual practice.

In the work reported in this paper the inversion coefficient of 0.514 for raffinose was used. The negative constituent of the Clerget divisor was taken as:

$$-(32.1 + 0.07\,g)$$

in which g is the grams of sucrose in the 0.5 N weight of sample taken for inversion, which is based on the negative inversion value of −33.00 for 100 per cent sucrose. Both constants are according to Browne and Gamble (*4*).

The negative constituent of the Clerget divisor was checked on solutions of pure sucrose, using the modified Walker method of inversion, as shown in Table VII. The agreement between the values found and those calculated from Browne and Gamble's formula for the given concentrations was considered satisfactory proof that the Browne and Gamble constants for the Herzfeld inversion procedure hold true when the inversion is made by the modified Walker method.

Table VII. Inversion Constant of Sucrose (Modified Walker Method)

(No lead acetate added)

Sucrose	Sucrose Used in Inversion	Observed in 400-mm. Tube	Calculated to 100 Sucrose	Browne and Gamble
%	*Grams*			
50.000	6.500	−16.27	−32.54	−32.56
88.089	11.451	−28.81	−32.71	−32.90
24.872	3.233	− 8.10	−32.57	−32.33
69.492	9.034	−23.75	−32.74	−32.73
50.098	6.513	−16.28	−32.50	−32.56
50.098	6.513	−16.24	−32.42	−32.56
88.493	11.504	−29.21	−33.01	−32.91
88.742	11.536	−29.20	−32.90	−32.91
		Av.	−32.67	−32.68

This basic negative constituent of −33.00 was determined by Browne and Gamble on pure sugar solutions, but the inversions in the double-acid method are made in the presence of the ammonium acetate and acetic acid resulting from the leading and deleading of the sample before inversion. This salt and acid were found to have a slight effect upon the inversion constant.

Sugar solutions of various concentrations were leaded and deleaded with the amounts of lead corresponding to the purity of a beet product of such sugar contents. For 50 per cent sugar, 20 ml. of lead acetate were used as in a molasses, proportionally less at higher sugar concentrations. The invert polarizations found are given in Table VII. The differences between the values found and those of Browne and Gamble for the given concentrations are also shown.

It would appear that the inversion constant, when made on leaded and deleaded solutions, is about 0.21 numerically less than when determined with pure aqueous solutions. The higher differences found with the 96 per cent solutions indicate that the inversion value becomes less as the sucrose concentration approaches 100.

If the results given in Table VII are accepted, the basic negative constituent becomes −32.79 instead of −33.00. Such a change in the Clerget divisor would lower a determined sucrose percentage by about 0.10. Since the adoption or rejection of this change in the inversion constant involves such a small difference in the analytical results, Browne and Gamble's −33.00 is used in the double-acid method. However, it is hoped that other data as to the effect of leading and deleading upon the inversion constants will be presented, for such data would be of general value and would probably apply to the enzyme as well as the acid formulas.

The raffinose inversion coefficient for the modified Walker inversion method was determined with the use of a very pure raffinose prepared by Hungerford and Nees. The results showed some variation and the average was a little lower than the Browne and Gamble value of 0.514. Fortunately, however, the structure of the Creydt formula is such that small variations in the raffinose coefficient have little effect upon the calculated sucrose or raffinose percentages. The value of 0.514 has been accepted and used in this work.

In the double-acid method the Clerget divisor is taken as proportional to the concentration of sucrose rather than dry substance. Several investigators have confirmed Vosburgh's rule (*13*) that the divisor is proportional to total sugar concentration and some prefer to make it proportional to dry substance in the analysis of an impure product. The authors have not been able to find any definite evidence in the literature that this divisor varies with the total dry substance of such materials as molasses. As the amount of raffinose in beet products is relatively small, it makes little difference whether it is considered in evaluating the divisor.

As is the case with the neutralization correction, for all general purposes the Clerget divisor may be taken as being proportional to the direct polarization P rather than S. However, dry substance may be used by those who prefer this basis.

The acid inversions from some molasses are so dark that it is difficult to read them with any reasonable degree of accuracy in the ordinary polariscope. Several methods of overcoming this are open to the analyst, such as using shorter polariscope tubes, more dilute solutions, or some decolorizer. The last mentioned has been chosen as introducing the least chance of error.

To insure inverted solutions of light enough color to permit accurate polarizations, 0.1 gram of sodium hydrosulfite is added when necessary to the invert solution just before adding the Clerget acid. This small amount of hydrosulfite has been found sufficient to decolorize the deleaded solution of even the darkest molasses without introducing any determinable error. Browne (*3*) mentions the objection to the use of this salt as a decolorizer, but he is speaking of greater amounts than the 0.1 gram used in this method. It has been found in a great many tests that this small amount of sodium hydrosulfite does not affect the invert polarization to any amount readable in the polariscope. In Table VIII some of the inversions were made with and some without this hydrosulfite, yet no different invert values were found.

Table VIII. Inversion Constant of Sucrose (Modified Walker Method) after Leading and Deleading

Sucrose	Sucrose Used for Inversion	Observed in 400-mm. Tube	Negative Polarization Calculated to 100 sucrose	Negative Polarization Browne and Gamble	Difference
%	*Grams*				
50.383	6.549	−16.30	−32.34	−32.56	−0.23
49.634	6.452	−16.05	−32.34	−32.55	−0.21
49.634	6.452	−16.05	−32.34	−32.55	−0.21
88.660	11.526	−28.99	−32.70	−32.91	−0.21
88.677	11.528	−28.98	−32.68	−32.91	−0.23
49.995	6.499	−16.22	−32.44	−32.56	−0.12
49.995	6.499	−16.20	−32.40	−32.56	−0.16
96.139	12.498	−31.53	−32.79	−32.97	−0.18
96.139	12.498	−31.38	−32.63	−32.97	−0.34
96.256	12.513	−31.38	−32.60	−32.98	−0.38
96.256	12.513	−31.43	−32.65	−32.98	−0.33
49.950	6.494	−16.15	−32.33	−32.55	−0.22
49.950[a]	6.494	−16.16	−32.35	−32.55	−0.20
49.950	6.494	−16.15	−32.33	−32.55	−0.22
49.950[a]	6.494	−16.18	−32.39	−32.55	−0.16
49.992	6.499	−16.18	−32.37	−32.55	−0.18
49.992[a]	6.499	−16.20	−32.40	−32.55	−0.15
49.992	6.499	−16.21	−32.42	−32.55	−0.13
49.992[a]	6.499	−16.18	−32.37	−32.55	−0.18
				Av.	−0.21

[a] With 0.1 gram of sodium hydrosulfite in the inversion.

Lead Precipitate Volume

As in any accurate analysis of an impure product, the double-acid method requires a correction for the volume of the lead precipitate. With most beet-sugar products, especially molasses, the error caused by this precipitate volume cannot be avoided by the use of dry lead acetate, as is the case with comparatively high-grade raw sugars which require a very small lead addition. With beet molasses it is customary to add 20 ml. of lead subacetate per normal weight of sample. The addition of an equivalent amount of dry lead would cause appreciable volume changes of which it would be impossible to take account.

Brown has found in numerous determinations by his centrifugalization method (*8*) an average value of 1 ml. for the precipitate volume of a normal weight of molasses clarified with 20 ml. of lead subacetate (55° Brix) and made to 100 ml. There is some variation in different molasses, but this is relatively small. Therefore in the analysis of molasses, 1 per cent of the sucrose and raffinose is deducted from the calculated percentages to correct for the concentration error resulting from this precipitate volume. Similar corrections should be made for other products according to the purity and amount of lead subacetate added. Corrections of the same kind should also apply in the double-enzyme method.

Impurity Effects

The impurities, other than the optically active nonsugars represented by the N value, may be termed the molasses impurities. Although presumably themselves optically inactive, they do affect the polarizations, both direct and inverted. This is what is sometimes called the salt or concentration effect. The literature presents very little information on this subject, yet it is fundamental. In the analysis of beet products by the double-enzyme method, Brown (*2*) has pointed out the desirability of attempting to eliminate the salt effect by always making the direct polarization at twice the concentration at which the invert polarization is made, because the Jackson and Gillis data (*5*) show that the effect of inorganic salts on the polarization of invert sugar is about twice that on the polarization of sucrose.

To obtain data on the magnitude of these effects, a Steffenized molasses was leaded and deleaded in the usual manner with basic lead acetate and ammonium phosphate, and all the raffinose and sucrose were then fermented off by repeated inoculations with bottom yeast, the alcohol being distilled off at reduced temperatures between fermentations. After four fermentations, the absence of sucrose and raffinose was confirmed by both invertase and melibiase inversions.

From this impurity solution and pure sucrose, a synthetic sirup of 60 purity containing approximately 50 per cent sucrose was prepared and analyzed. The results were surprising.

The analysis of the synthetic mixture gave the following results as compared with the calculated values for the sucrose alone. The acid invert value was arithmetically decreased by 0.95° S. The observed direct polarization was lowered 0.83° S. When corrected for the determined N value, the direct polarization was increased 1.09° S.

The impurities evidently move both the invert and corrected direct polarizations to the right by approximately equivalent amounts. However, when the raffinose formula is applied, the calculated percentage of sucrose is decreased by about 0.46. The net effect therefore tends to give sucrose results that are falsely low.

Paine and Balch (*9*) found the direct polarization to be decreased by the addition of nonsugar molasses impurities to a smaller extent than the invert is increased. This appears to be in contradiction to the writers' observations, but is not necessarily so. Paine and Balch were considering the total effect of the impurities, including the depressing influence of the optically active nonsugars or N value, which was doubtless a negative value. The authors also found the total effect to decrease the direct polarization, but after correcting for the determined N value the net effect was to increase the polarization. It is probable that the same actually held true with the impurities used by Paine and Balch. The effects upon the inversions cannot very well be compared, because Paine and Balch used enzymes while the authors' results were on acid inversions. If the enzyme inversion values are shifted to the right to the same extent as the direct, no error is introduced in the resulting sucrose by the enzyme formula, because this is dependent upon the difference between the direct and invert polarizations. Further investigation is needed to determine the net effect of the molasses impurities upon the enzyme method.

Since all the single-acid inversion methods give lower sucrose percentages than the double-acid method, the fact that the double-acid apparently gives results that are slightly low on low-purity products makes the case against the methods in common use even more pronounced.

This work on molasses impurities has not progressed to the point where any change in the acid inversion constants is suggested. Further work is now in progress. For the time being this salt or concentration effect of the molasses impurities is therefore ignored in the double-acid method, which is also true of all acid inversion methods.

Details of Double-Acid Method

The double-acid method gives three determined polarizations, the direct (P), the invert read in the acid solution (I), and the neutralized invert (I'). After applying the proper neutralization correction to I', the algebraic difference between I and the corrected I' is the polarizing effect of the nonsugars, or N. This is generally a negative value and when subtracted algebraically from P gives what the direct polarization would have been if it had not been affected by the N value. This corrected direct polarization, designated P', is then the polarization of the sucrose plus raffinose and may be used in the usual Clerget formula in conjunction with I to calculate the sucrose and raffinose percentages.

Several different formulas may be set up on this basis to calculate a double-acid analysis. As presented here, the Clerget divisor is taken to vary with the sucrose concentration, or with the direct polarization as approximately representative of the total sugars present. If desired, it may be taken as proportional to dry substance. The same may be said of the neutralization correction K in the formulas as taken from Table VI.

The double-acid method in detail may be given as:

Transfer 130 grams of the sample, or its equivalent, to a 500-ml. Kohlrausch flask, add the necessary basic lead acetate, and make to 400 to 450 ml. with water. Deaërate under vacuum until all visible gas bubbles are removed, using a few drops of ether or amyl alcohol to break the foam if necessary. Make to 500 ml. at 20° C., mix, and filter. Delead the filtrate with the minimum of powdered ammonium dihydrogen phosphate, and filter, using a little filter aid if desired. Polarize in a 200-mm. tube to obtain the direct polarization P.

Pipet 50 ml. of the deleaded filtrate into each of two 100-ml. Kohlrausch flasks. Add 15 ml. of water and heat to 68° to 69° C. in a 70° C. water bath. Remove from bath and immediately add 10 ml. of hydrochloric acid (d_4^{20} 1.029). Allow to cool spontaneously for 2 hours and then cool to 20° C. Make the one invert to 100 ml. at 20° C., mix, filter if necessary, and polarize at 20° C. in a 400-mm. tube, the reading being the invert polarization I. To the second invert add 1 or 2 drops of 0.2 per cent methyl red indicator solution and neutralize with 6.34 N ammonium hydroxide, adding the ammonia very slowly from a buret while constantly whirling the flask. Then add exactly 1 ml. in excess. Make to 100 ml. at 20° C., filter if necessary, and polarize in a 400-mm. tube, to obtain the neutralized invert polarization I'.

The N value, sucrose, and raffinose are then calculated by the formulas:

$$N = I' - I + K$$
$$P' = P - N$$
$$S = \frac{0.514\,P' - I}{0.514 + (0.321 + 0.00009\,S)} = \frac{0.514\,P' - I}{0.835 + 0.00009\,S}$$
$$\text{or } \frac{0.514\,P' - I}{0.514 + (0.321 + 0.00009\,P)} = \frac{0.514\,P' - I}{0.835 + 0.00009\,P}$$
$$R = 0.54\,(P' - S)$$

where N = polarizing effect of the optically active nonsugars
P' = true direct polarization of the raffinose and sucrose
S = per cent sucrose
R = per cent raffinose
K = neutralization correction, to be obtained from Table VI as proportional to either S or P and milliliters of lead used per 100 ml. of leaded solution

The following notes on the technic of the method may be of value:

1. If amyl alcohol is used to break the foam while deairing, do not use more than 3 or 4 drops, because this alcohol is optically active and is not volatile at room temperatures.
2. Make all filtrations under wetted bell jars resting on wetted rubber mats, or with the filters covered with large cover glasses. Discard the first 10 to 15 ml. of each filtrate.
3. The amount of ammonium phosphate necessary to delead may be determined by adding small incremental amounts and testing for complete precipitation by testing a drop with a solution of potassium iodide or with a further crystal of ammonium phosphate. An undue excess of phosphate must be avoided, for each 1 gram excess per 100 ml. depresses the direct polarization 0.35° S.
4. As much as 0.1 gram of sodium hydrosulfite may be added with the inverting acid if the solution is dark.
5. The calculated percentages of sucrose and raffinose should be corrected for the volume of the lead precipitate. In molasses this may be done by deducting 1 per cent of the calculated percentage from itself. This correction will be proportionately less on higher purity products, varying with the decrease in impurities and amount of lead acetate used.

Acknowledgments

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Determination of Minute Quantities of Sulfide Sulfur

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The method developed in the western branch laboratory of the National Canners Association for the determination of small quantities of volatile sulfide sulfur is a modification of that described by Drushel and Elston (*3*). The principal differences are in the method of evolution and the type of apparatus used in collecting the stain on the lead acetate paper. The sulfide gas upon evolution from an acid solution is continuously carried along and through a lead acetate–impregnated paper diaphragm by a stream of an inert gas such as nitrogen. The nitrogen, by intimately diluting the sulfide gas, permits a uniform coating of lead sulfide and sweeps the reaction flask free from residual sulfide gas. A uniform deposition of the stain is further aided by means of a 1- to 2-inch (2.5- to 5-cm.) bed of small glass beads or standard Ottawa sand. The impregnated paper disk is closely fitted between two ground-glass joints of thick-walled glass tubing which are held together by a band of Gooch rubber tubing so that all gas leaving the reaction flask must pass through the paper.

Under the conditions of the experiment sulfur dioxide does not interfere and only the sulfide which is evolved by acid is determined. The diameter of the chamber tube employed is governed by the amount of sulfide present. For amounts of volatile sulfide sulfur between 0.008 and 0.080 mg. a 32-mm. tube was found to be satisfactory, and under these conditions an accuracy of ±0.002 mg. of sulfur is possible. The delicacy of the test is increased by using chamber tubes of smaller diameter.

Standards

The paper found to give good results was Schleicher and Schull No. 589 black ribbon filter paper. It is sensitized by soaking for one hour in a saturated neutral lead acetate solution and air-dried by vigorous waving, followed by an air blast. The paper may then be cut in disks to fit the appropriate chamber tube. Indications are that impregnated paper will retain its sensitivity for several months if kept protected in a closed container.

Standard stains are prepared by evolving the sulfur from weighed samples of Bureau of Standards steels such as No. 14b basic open hearth steel containing 0.031 per cent of volatile sulfur. This method of standardization was found preferable to the usual practice of diluting strong standard sodium sulfide solutions, as the dilution necessary to obtain small amounts of the standard resulted in immediate oxidation of some of the sulfur.

After deposition of the lead sulfide stain the disks are thoroughly washed in distilled water and dried between sheets of white blotting paper. They are preserved by keeping them in the dark while not in use, as oxidation to colorless lead sulfate occurs when exposed to sunlight, particularly in the case of very faint stains.

Method

The sample is placed in a 1000-cc. Erlenmeyer flask with about 100 cc. of distilled water and the system swept with nitrogen to remove excess air, after which 50 cc. of 1 to 1 hydrochloric acid

(special arsenic-free hydrochloric acid gives a perfect blank for this work) are added by means of a dropping funnel. Some operators may prefer to use 100 cc. of 1 to 1 phosphoric or sulfuric acid to eliminate the necessity for a moist cotton plug for absorbing any escaping hydrochloric acid fumes. The contents of the flask are heated to boiling and a stream of nitrogen (about 5 mm. of pressure) is continually passed through the system until all sulfide has been evolved. The residual gas is washed out of the flask by increasing the nitrogen stream (to about 30 mm. pressure) during the last 2 minutes of the determination. The disk is then removed, washed in distilled water, dried, and compared with the standards. For small quantities direct comparisons of color can be made, but with the heavier deposits it is necessary to compare with standards by holding them in front of a source of light.

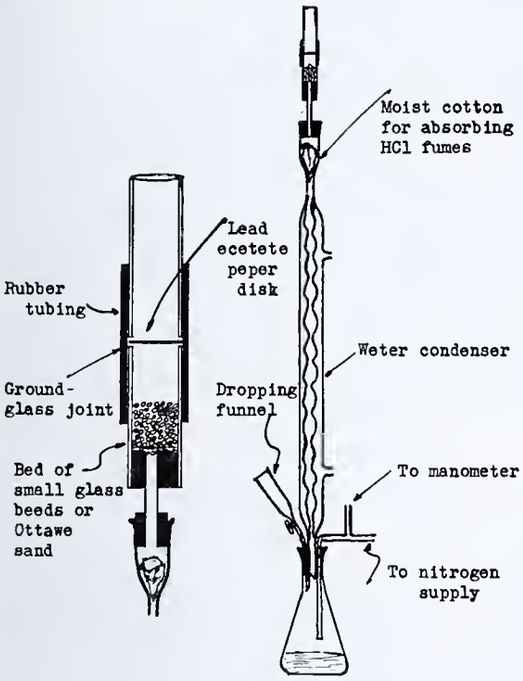

FIGURE 1. DIAGRAM OF APPARATUS

APPLICATIONS OF METHOD

This method has been found useful in this laboratory in the analysis of foodstuffs, including raw and canned products, and for the determination of very small quantities of sulfide sulfur in water. In the case of water it is capable of estimating minute amounts by acidifying a large volume of the sample and passing the evolved gas through a chamber tube of small diameter. When samples cannot be examined at the source, the method cited by Collins (*2*), using crystalline cadmium chloride to preserve the sulfur from oxidation, can be used. The resulting precipitate may thus be examined for sulfide content at the convenience of the analyst by acidifying the precipitate in the reaction flask and proceeding as in the preparation of standards.

During a recent investigational study this laboratory had occasion to determine the amount of sulfide stain imparted to the inside of tinned containers by different food products. As the tin itself contains an appreciable amount of sulfide sulfur, a stripping solution was developed that would remove only the stain and not extract sulfur from either the tin or the base plate. The sample was immersed for 2 minutes in 25 cc. of a boiling solution consisting of 20 cc. of 1 per cent sodium hydroxide solution and 5 cc. of 40° Be. sodium silicate, followed by washing with distilled water. The alkaline solution of sulfide was then transferred to the 1000-cc. flask, swept with nitrogen, acidified, and the sulfur determined as in standards.

The sulfur content of tin coatings can be determined by the disk method to a fair degree of accuracy by the use of large disk chambers. The stream of nitrogen should be greatly increased to insure intimate dilution of the hydrogen sulfide generated. The depth of the filter (Ottawa sand or small glass beads) should also be increased to about 3 inches (7.5 cm.) in order to insure an even deposition of stain on the larger disk. Instead of using the lead plumbite method of stripping tin from tin plate, a method developed by Bohart (*1*) is used in this laboratory. In this method a tin-plate disk (area 4 sq. in., 25.8 sq. cm.) is placed in a beaker containing about 25 cc. of 1 per cent sodium hydroxide solution, the surface of the disk being sprinkled with pieces of cupric oxide wire. Solution of the tin, excluding that in the alloy layer, is effected in about 2 hours at room temperature, whereas a hot solution accomplishes this reaction within a few minutes. The action may be accelerated at both temperatures if desired, by increasing the concentration of sodium hydroxide. After thoroughly rinsing the disk, the solution is filtered and transferred to the generating flask, where the sulfide is evolved and estimated.

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RECEIVED December 28, 1933.

A Micro Hot-Plate for Protein Hydrolysis

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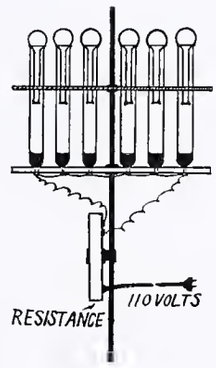
SMALL samples (0.1 gram) are hydrolyzed in 6 × 0.75 inch (15.2 × 1.9 cm.) test tubes. A micro hot-plate supplies heat to each test tube. The reflux condensers are 3 × 0.375 inch (7.6 × 0.95 cm.) test tubes, a bulb blown on the end of each, resting inverted in the large test tubes. The method results in efficient condensation in an all-glass system, uniform heating, and fool-proof simplicity. With it tryptophane was determined in sixty samples with a probable error of 0.05 per cent.



SET-UP OF APPARATUS

Each test tube rests upon a flat spiral of 6 inches (15.2 cm.) of 30-gage Chromel wire. The spirals are bolted to an asbestos board, in series with a rheostat or suitable resistance. The test tubes are held upright by the cross-piece from a test tube rack, the six holes being directly over the six hot spirals. The cross piece, the asbestos board, and the resistance are supported on a ring stand by three buret clamps.

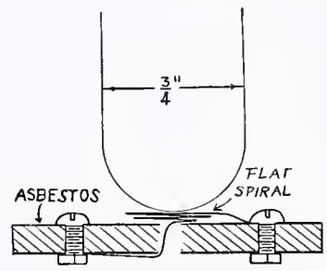


DIAGRAM OF HOT-PLATE

RECEIVED March 2, 1934.

Rapid Centrifugal Estimation of Small Amounts of Sodium

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SEVERAL workers have shown that small amounts of sodium can be determined with fair rapidity through precipitation as a triple uranyl acetate, either by weighing the precipitate or by dissolving it and applying suitable volumetric or colorimetric procedures. However, where a large number of samples must be examined in a short period, as in biochemical investigations, a very rapid method for estimating small amounts of sodium would seem desirable, even though it involved some loss in accuracy. It has been found that measuring the amount of a precipitate by collecting it in a capillary tube under centrifugal force and reading the volume leads to a satisfactory solution of the problem, since triple acetate precipitates are not only voluminous but, under proper conditions, can be obtained in minute uniform particles that pack in capillary tubes in a readily reproducible manner.

Apparatus

The centrifuge made by the International Equipment Co., designated as Size 1, Type C, was used throughout the experiments. It was provided with a standard head having places for two carriers designed to hold Goetz phosphorus tubes. A special tube was also used, provided with a capillary of similar length but of smaller internal diameter for experiments with precipitates too small in amount to permit accurate reading of their volumes in the 0.20-cc. capillaries of the Goetz tubes. This special tube was made by removing the capillary from a Goetz tube and attaching one with a uniform internal diameter of approximately 1.5 mm. and a length of 35 mm. The lower end of this capillary was sealed off squarely to avoid reading errors that might originate from a rounded or tapering bottom, for instead of graduating and calibrating the tube in the usual manner it was found simpler, and just as satisfactory, to measure the lengths of the columns of collected precipitate by means of a millimeter scale. The Goetz tubes, however, were calibrated for each etched 0.01-cc. interval with mercury. A simple and convenient tool for removing packed precipitates from the capillaries was made by giving a screw-shaped twist to the flattened end of a short length of stiff wire. Thin pipets made by drawing out glass tubing were also found convenient in cleaning the capillary tubes. The more usual apparatus used in the experiments requires no special description.

Reagent and Solutions

An aqueous reagent was not found practical for these determinations, since comparatively large crystals varying somewhat in size are formed by precipitation in an aqueous system, and these fail to pack in a sufficiently consistent and reproducible manner in capillary tubes. On the other hand, an alcoholic reagent produces minute and uniform crystals, probably because of the more rapid precipitation of the triple acetate in a medium that markedly decreases its solubility. By slightly modifying an alcoholic magnesium uranyl acetate reagent recommended by Kahane (*3*), a satisfactory precipitant was produced.

For the preparation of a liter the following quantities are required: uranyl acetate ($2H_2O$), 30 grams; magnesium acetate ($4H_2O$), 150 grams; acetic acid (99 per cent), 20 cc.; and ethyl alcohol (95 per cent), 500 cc.

These chemicals are weighed into a flask and sufficient water is added to make the total volume slightly less than a liter. The mixture is then heated on a steam bath until practically all salts are in solution. On cooling to room temperature the volume is adjusted to 1 liter, and the solution allowed to stand at the subsequent working temperature for several hours. The temperature is controlled, if necessary, by placing the flask in a vessel of water. During the standing period the solution should be stirred or shaken at intervals to facilitate the complete precipitation of excess salts. The reagent is finally filtered into a reagent bottle of brown glass.

The sodium, potassium, and lithium solutions employed in the experiments were prepared by dissolving given amounts of the pure chlorides in water and adjusting to the proper volumes in volumetric flasks.

Preliminary Experiments

A number of experiments were made to determine the effects of different conditions during precipitation on constancy of precipitate volume. The factors considered were temperature, relative volumes of sodium solution and reagent, the order and method of mixing solution and reagent, agitation and nonagitation during precipitation, and time allowed for precipitation. Likewise the effects of different speeds and times of centrifugalizing on the final volumes occupied by precipitates were studied, together with the rates at which these volumes were attained.

Procedure

Mount a clean dry centrifuge tube of suitable type in an upright position under a motor stirrer fitted with a thin stirring rod, and if necessary provide for approximate temperature control by partly immersing the tube in a beaker of water maintained at the desired temperature. Place 10.0 cc. of reagent in the tube by means of a pipet, followed by 2.00 cc. of the unknown solution, containing not more than about 2 mg. of sodium, likewise added with a pipet. Immediately mix the two solutions and stir for 10 minutes at such a rate that little or no precipitate settles out. Without rinsing off the stirring rod, remove the tube, stopper it, and place it in a previously counterbalanced centrifuge tube carrier. Centrifugalize immediately at some definite speed between 1600 and 2000 r. p. m. for 10 minutes, and then for a few successive 3-minute periods until a constant precipitate volume is reached. Standardize the tube with known amounts of sodium in the form of a standard sodium chloride solution, using the same procedure.

Unless the centrifuge vessel is thoroughly cleaned before use the precipitate adhering to the upper walls of the tube may cause difficulty. The precipitate will be completely thrown into the capillary, however, if the vessel is cleaned with dichromate mixture, washed with water, rinsed with alcohol, and finally dried in an oven at 100° to 110° C. to remove the alcohol from the capillary. In cleaning the capillary the successive liquids are best introduced by thin pipets, after removing any previous precipitate by means of the wire tool described above.

While precipitations made with an aqueous magnesium uranyl acetate reagent require rather close temperature control, this is not so essential with a reagent of the type used in this procedure, largely because of the much decreased solubility of the triple acetate in strong alcoholic solutions. Approximate temperature control is required only when the room temperature is more than 4° to 5° C. from the temperature at which the reagent was prepared, for only in this

case is there danger of erratic results from increased or decreased precipitation.

It is essential that the reagent be added to the centrifuge vessel first, for a reversal of this order may lead to erroneous results due to trapping of sodium solution in the capillary where it can escape precipitation during stirring. The recommended volumes of reagent and solution were chosen on the basis of a series of experiments as being most generally suitable for the practically complete precipitation in a short time of the small amounts of sodium covered by the range of the procedure. The sodium solution is to be added ordinarily as an aliquot portion of some known volume prepared in a small volumetric flask or graduated tube.

Immediate mixing of solution and reagent is necessary in order to avoid erratic variations in precipitate volumes which may be caused, under conditions of relatively low alcohol and salt concentrations, by the formation of larger particles than those formed rapidly in the thoroughly mixed solutions where concentrations are uniformly high. Precipitation by simply allowing the mixed solutions to stand, or combinations of standing and stirring, were found to lead to unsatisfactory results, both because of the increased time needed for complete precipitation and because less reproducible precipitate volumes were obtained. The latter effect was ascribed to the formation of larger, less uniform precipitate particles than those produced by immediate rapid stirring. The nonsettling of the precipitate during stirring serves as an index of a stirring rate sufficient to bring about practically complete precipitation in the stated time. Furthermore, less uniformly packed precipitates are obtained on centrifugalizing if more than a small fraction of the precipitate is allowed to settle in the capillary during stirring. By the use of a sufficiently thin stirring rod a negligible portion of the precipitate is left on it upon removal from solution; no time need be lost in cleaning off the stirrer, and errors that might be introduced by the use of wash liquids are avoided. A rod about 1.5 to 2.0 mm. in diameter provided with a short 45° bend at the tip, to be immersed below the surface during stirring, is satisfactory, and also provides efficient stirring without danger of loss from splashing.

It is important to employ the same centrifuge speed for all standardizations and determinations, in order to obtain the same degree of packing in all individual precipitates. With the type of centrifuge and head used in the experiments, speeds of 1600 r. p. m. or above are preferable, in that the triple acetate precipitates then pack to a constant volume in a very short time as compared with available lower speeds. With tubes and carriers of the usual type speeds above 2000 r. p. m. are not advisable by reason of the danger of breakage.

Frequently, the upper surface of a packed precipitate is not quite level after the first period of centrifugalizing. This source of difficulty in reading the volume may be remedied by stirring the high part of the surface layer of the precipitate with a stiff wire before recentrifugalizing.

With the usual two- or four-place centrifuge head and a corresponding number of calibrated tubes, it is possible to make a like number of determinations at the same time, provided enough motor stirrers are available to make precipitations simultaneously prior to centrifugalizing. This is necessary in order that the individual samples may be subjected to identical treatment, which is one of the chief requirements in this type of analysis.

Results with Sodium Solutions

Typical results obtained by the above procedure, using a Goetz tube and sodium chloride solutions of known value, are shown in Table I. The tube was standardized by using the average precipitate volume found in the case of the six 2.00-mg. samples. Expressed on a unit basis, a quantity of triple acetate precipitate corresponding to 1.00 mg. of sodium thus occupies an average volume of 0.078 cc. This value was then used to convert the volume readings of all the individual trials into milligrams of sodium. The results are, in general, satisfactory from the viewpoint of the difference errors, especially if the averages are considered. The percentage errors are more than could be tolerated with larger amounts of sodium, but with the quantities involved here these deviations are not serious, inasmuch as the procedure is not intended for a micromethod; in fact, the results compare favorably with those obtainable gravimetrically on similar amounts. With the Goetz tube, about 2.5 mg. of sodium are the maximum that can be determined. Somewhat larger amounts could be estimated by means of a longer or wider capillary, but upward extension of the range would probably incur a corresponding loss of accuracy. Because of the rounded lower end of the capillary on the standard Goetz tube and its diameter, the estimation of amounts of sodium below 0.2 mg. involves considerable uncertainty due to reading errors.

Table I. Estimations of Sodium with Goetz Tube

Sodium Taken	Final Volume of Precipitate	Sodium Found	Difference Error
Mg.	*Cc.*	*Mg.*	*Mg.*
2.00	0.162	2.08	+0.08
2.00	0.160	2.05	+0.05
2.00	0.155	1.99	−0.01
2.00	0.161	2.06	+0.06
2.00	0.148	1.90	−0.10
2.00	0.150	1.92	−0.08
1.00	0.080	1.03	+0.03
1.00	0.079	1.01	+0.01
1.00	0.081	1.04	+0.04
1.00	0.080	1.03	+0.03
1.00	0.076	0.97	−0.03
1.00	0.078	1.00	±0.00
0.50	0.042	0.54	+0.04
0.50	0.042	0.54	+0.04
0.50	0.039	0.50	±0.00
0.50	0.042	0.54	+0.04
0.20	0.016	0.21	+0.01
0.20	0.013	0.17	−0.03
0.20	0.015	0.19	−0.01
0.20	0.013	0.17	−0.03

Table II. Estimations of Sodium with Special Centrifuge Tube

Sodium Taken	Final Length of Precipitate Column	Sodium Found	Difference Error
Mg.	*Mm.*	*Mg.*	*Mg.*
0.50	26.0	0.52	+0.02
0.50	24.0	0.48	−0.02
0.50	23.5	0.47	−0.03
0.50	26.5	0.53	+0.03
0.20	9.0	0.18	−0.02
0.20	9.0	0.18	−0.02
0.20	8.7	0.17	−0.03
0.20	10.0	0.20	±0.00
0.10	4.0	0.08	−0.02
0.10	3.5	0.07	−0.03
0.05	1.0	0.02	−0.03
0.05	1.3	0.03	−0.02
0.10[a]	5.0	0.10	±0.00
0.10[a]	5.3	0.11	+0.01
0.05[a]	2.5	0.05	±0.00
0.05[a]	2.0	0.04	−0.01

[a] In these cases the sodium solutions were reduced to a volume of 1.0 cc.

In order to examine more closely the degree of accuracy obtainable by this centrifugal method when dealing with only a few tenths of a milligram of sodium, a number of determinations were also made by means of a special tube, the construction of which has been described above. These results are shown in Table II. In this series the average of the readings obtained with the 0.50-mg. quantities was used to standardize the tube, so that 1.0 mm. in length of precipitate column was considered as representing 0.02 mg. of sodium in all the individual trials. When the amount of sodium being estimated is about 0.1 mg. or less, incomplete

precipitation due to the solubility of the precipitate becomes appreciable. This can be remedied either by using a lesser volume of sodium solution, as shown in the last four determinations, or by standardizing the tube at intervals with like small amounts of sodium instead of on the basis of a single larger quantity. With the procedure given, 0.05 mg. of sodium appears to be about the smallest amount that can be precipitated successfully. In general, in the case of samples containing only a few tenths of a milligram of sodium the use of a centrifuge vessel with a somewhat narrower capillary than that of the Goetz tube leads to more satisfactory results.

Influence of Other Ions

Owing to the lack of quantitative data in the literature concerning interference effects with a reagent of the type required in this method, experiments were also made to determine the permissible limits of elements like potassium and lithium that normally accompany sodium. Instead of determining these limits by the more usual methods the centrifugal method was considered more suitable for the immediate purpose, since by this means not only could the usual co-precipitation effects be studied, but also any possible influence of foreign ions on the volumes of precipitates due merely to changes in particle size. The above procedure was applied, therefore, to 2.00-cc. samples of chloride solutions containing varying amounts of foreign ion alone, or with added fixed amounts of sodium. The results are set forth in Tables III and IV. It is apparent that potassium and lithium interfere seriously when present in sufficiently high concentration, probably because of the formation of the corresponding double uranyl acetates, with resultant increase in precipitate volume over the normal value. Lower concentrations of potassium or lithium apparently do not change the particle size or volume of the sodium precipitate. Contamination of the sodium precipitate increases with rise in amount of sodium being precipitated, in accordance with the usual co-precipitation effect. Somewhat more than 5 mg. of potassium may be present if the amount of sodium being determined lies in the lower part of the range covered by the method, but not when higher amounts of sodium are being precipitated. In general the use of an alcoholic instead of an aqueous reagent for direct sodium determinations results in considerably increased interference from potassium (*1*, *2*). This is not serious enough, however, to prevent the use of this centrifugal method for most samples of natural products, since the potassium-sodium ratio in such materials is not often high.

Table III. Effect of Presence of Potassium

Potassium Present	Sodium Taken	Amount of Precipitate	Apparent Amount of Sodium Found	Difference Error
Mg.	*Mg.*	*Mm.*	*Mg.*	*Mg.*
5.0	0.00	0.0	0.00	±0.00
10.0	0.00	0.0	0.00	±0.00
15.0	0.00	0.5	0.02	+0.02
20.0	0.00	3.0	0.08	+0.08
5.0	0.10	3.7	0.09	−0.01
5.0	0.10	4.3	0.11	+0.01
7.5	0.10	4.5	0.11	+0.01
7.5	0.10	4.0	0.10	±0.00
10.0	0.10	6.0	0.15	+0.05
10.0	0.10	5.5	0.14	+0.04
		Cc.		
3.0	1.00	0.078	1.00	±0.00
3.0	1.00	0.076	0.97	−0.03
5.0	1.00	0.085	1.09	+0.09
5.0	1.00	0.088	1.13	+0.13
10.0	1.00	0.097	1.24	+0.24
10.0	1.00	0.092	1.18	+0.18

Lithium interferes only slightly more than potassium. There is much less discrepancy between interference effects with the alcoholic and aqueous types of reagent in the case of lithium. With other ions the alcoholic reagent was found to react in essentially the same manner as the aqueous type, but it may sometimes cause difficulty in the presence of substances readily precipitated by dilute alcohol. This source of interference may obviously be circumvented by treating the sample solutions with alcohol and filtering before further preparing them for the addition of the reagent, provided that sodium is not removed by such an operation.

Table IV. Effect of Presence of Lithium

Lithium Present	Sodium Taken	Amount of Precipitate	Apparent Amount of Sodium Found	Difference Error
Mg.	*Mg.*	*Mm.*	*Mg.*	*Mg.*
5.0	0.00	0.0	0.00	±0.00
10.0	0.00	1.0	0.04	+0.04
15.0	0.00	4.5	0.11	+0.11
20.0	0.00	5.5	0.14	+0.14
5.0	0.10	4.0	0.10	±0.00
5.0	0.10	3.5	0.09	−0.01
7.5	0.10	5.0	0.13	+0.03
7.5	0.10	5.7	0.14	+0.04
10.0	0.10	6.0	0.15	+0.05
10.0	0.10	7.0	0.18	+0.08
		Cc.		
3.0	1.00	0.078	1.00	±0.00
3.0	1.00	0.080	1.03	+0.03
5.0	1.00	0.088	1.13	+0.13
5.0	1.00	0.094	1.21	+0.21

Table V. Test Analyses of Waters

Sample	Sodium Content	Determination	Tube Readings	Sodium Found	Errors
	P. p. m.		*Mm.*	*P. p. m.*	*P. p. m.*
A	10.0	1	10.0	10.0	±0.0
		2	10.3	10.3	+0.3
		3	10.0	10.0	+0.0
		4	9.3	9.3	−0.7
			Av. 9.9	9.9	−0.1
B	18.8	1	22.3	17.8	−1.0
		2	24.0	19.2	+0.4
		3	23.5	18.8	±0.0
		4	23.0	18.4	−0.4
			Av. 23.2	18.6	−0.2

Sample A, synthetic water made from pure salts, contained the following ions in parts per million: Ca, 50; Mg, 20; Na, 10; K, 5; Li, 5; NH_4, 1; Fe, 1; Cl, 120; SO_4, 21.

Sample B, artesian well water from Princeton, N. J. The sodium content was determined gravimetrically by evaporation of a 250-cc. portion and application of the usual magnesium uranyl acetate method.

Test Analyses

In order to test its practicality this centrifugal procedure was also applied to several complex samples of known sodium content. Among these were two waters, the one a synthetic mineral water with a purposely exaggerated potassium and lithium content, the other a natural water in which the sodium had been carefully determined gravimetrically. The results are shown in Table V. For the analysis of sample A, 500 cc. of the water, acidified with hydrochloric acid, were first evaporated to dryness in a platinum dish. The residue was then dissolved in distilled water and the resulting solution adjusted to a volume of 50.0 cc. in a volumetric flask. Aliquot portions of 2.00 cc. were withdrawn for each determination, which was performed with the special centrifuge tube. This method of reducing the volume was used in order that each millimeter of precipitate column might represent 1 p. p.m. of sodium in the original water on the basis of the previous calibration of this tube. The results are satisfactory, although there is a certain compensating error involved in this good agreement, since the volumes of the precipitates are slightly larger than they should be for the calculated 0.20 mg. of sodium present in each sample. Table II shows that this amount, when precipitated from pure sodium solutions, produced precipitate columns with an average length of 9.2 mm. The small average additional volume obtained in the case of the water samples was found to be due to a slight contamination of the sodium precipitate with calcium sulfate precipi-

tated by the alcoholic reagent. However, this source of error does not appear serious. In the analysis of sample B separate volumes of the water were concentrated in platinum for the individual determinations, and each 2.00-cc. sample used in the procedure represented 25.0 cc. of the original water. The results agree satisfactorily with the gravimetric value, which is itself probably close to the truth.

Trial determinations on samples of milk indicated that the method could also be applied with success to biological material after suitable preliminary treatment to remove organic matter and phosphates. Oxidation with hot concentrated nitric acid in a quartz vessel was used to eliminate organic matter, while the addition of a slight excess of uranyl acetate reagent to a dilute solution of the ash, previously made slightly acid with acetic acid, served to remove the phosphate. The filtrate from the uranyl phosphate was then adjusted to a suitable volume and aliquot portions were used for the determinations.

Conclusions

The centrifugal method appears well adapted to the rapid estimation of small amounts of sodium in a variety of materials, especially for routine use on a long series of samples of a similar nature. Results can be rapidly obtained, especially when sets of tubes and carriers are used for two or more simultaneous determinations.

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Determination of Pentosans in Vegetable Materials Containing Tannins

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When the pentosan content of cottonseed hulls or burrs is estimated according to the usual Tollens method, low results are obtained. The decrease in pentosan yield ranges from 2.50 to 47.0 per cent, depending upon the amount of tannins contained in the material to be tested, as well as its condition. The influence of tannins on the determination of pentosans is particularly important in the case of hulls damaged in storage.

In addition to the effect of tannins on the furfural yield during distillation according to Tollens, lignin probably also exerts an influence, but it failed to be proved by experiment.

To gain a correct idea of pentosans in cottonseed hulls, in addition to the determination of xylose from hulls by means of acid hydrolysis according to Tollens, determination of pentosans in the hull residue should be carried out. The total of both determinations gives a more accurate idea of the pentosan content in the original material.

The pentosan content of vegetable materials is usually determined by the Tollens method. However, it is necessary to follow the standard procedure strictly, any deviation leading to erroneous results (*2*, *3*).

The principal defects of the method are:

1. The impossibility of distinguishing among individual pentosans, all forming furfural with hydrochloric acid.
2. Furfural may also be formed from substances such as galactan and galacturonic or glucuronic acids, which are components of pectin substances.
3. Should the substance to be tested contain sugars other than pentosans, methylfurfural would be formed from methyl pentosans (fucose, ramnose). ω-Oxymethylfurfural is obtained from a number of hexoses—glucose, mannose, galactose, fructose—hence also from starch, cellulose, and other polysaccharides from which these sugars are formed by hydrolysis. Because furfural derivatives—methylfurfural and ω-oxymethylfurfural—are also obtained, the determination is very difficult.

Other defects of the method are the variable composition of the condensation product of furfural with phloroglucinol, its solubility in acid solution, etc.

No data were found in the literature concerning the influence on the yield of furfural, and hence on the results of the determination of pentosans of components of plant tissue, which under no conditions form furfural by themselves. The aim of the present work is to ascertain the influence of such components, using cottonseed hulls and burrs.

Sources of Furfural Loss

Attention was first drawn to the fact that cottonseed hulls contain tannins. When tannins are boiled with furfural and hydrochloric acid, insoluble condensation products are obtained. This is the basis of the method used in the analysis of tannins, or the so-called Lauffmann's furfural precipitation numbers, whereby the highest figures are obtained for pyrocatechol tanning substances, which include the tannin of cottonseed hulls. In fact, when an aqueous extract of cottonseed hulls was heated with furfural under the conditions of Lauffmann's reaction, insoluble condensation products of furfural with tannin were readily formed. It is more than probable that such condensation takes place when furfural is obtained from materials containing tannins, which obviously leads to a considerable decrease in the yield of furfural.

The second source of losses in the yields of furfural may be another condensation reaction, occurring under conditions similar to those that take place when pentosans are determined according to Tollens—the condensation of furfural with lignin (*4*). Hulls contain 30 per cent of lignin. When furfural is boiled with lignin and hydrochloric acid, chemically inert resinous substances are formed. It is possible that tannins and lignin cause the decrease in yield of furfural when analytically determined. This suggestion agrees with the data obtained by Freudenberg and Harden (*1*), which show

that, when lignin is treated with hydrochloric acid, formaldehyde is formed, is precipitated in the distillate by phloroglucinol, and forms the precipitate which by its relation to alcohol resembles methylfurfuralphloroglucide and oxymethylfurfuralphloroglucide; because of this the determination of pentosans in wood should give too high results.

Freudenberg and Harden, however, obtained only 0.6 to 0.8 per cent as phloroglucide, instead of 2 per cent of formaldehyde. The remainder, in their opinion, is fixed by protocatechuic acid liberated during the reaction.

Under the authors' experimental conditions no increase in the phloroglucide yield was caused by the formation of formaldehyde. This may be accounted for by the presence of tannins and related insoluble phlobaphenes. On the other hand, the alcohol-soluble fraction was in no case present in the precipitate in appreciable amount. This leads to the conclusion that the influence of lignin on the determination lies mostly in the formation of insoluble condensation products with furfural. Freudenberg and Harden, however, worked with pure lignin, containing no pentosans.

Experimental

The first problem was to prove experimentally the existence of such an influence. For this purpose hulls from one oil mill (1929) stored in the laboratory were used. Table I shows the chemical analysis of these hulls.

Table I. Chemical Analysis of Hulls

Determination	%	Determination	%
Pure cellulose	45.82	Alcohol extract	0.54
Pentosans in hulls	12.02	Water extract	8.54
Methyl pentosans	Traces	Tannins in water extract	3.94
Lignin	23.71	Nitrogen general	0.63
Ether extract	0.65	Ash	1.79

As will be noted, the determination according to Tollens showed that pentosans formed 12.02 per cent of the weight of hulls. In comparing these results with other data their correctness seemed doubtful, because it is known that 26 per cent of xylose can be obtained from cottonseed hulls which contain 29.9 per cent of pentosans. There are also indications that hulls may contain up to 37.9 per cent of pentosans.

It was decided first to check the contents of pentosans in the sample in an indirect way. It was necessary to remove the tannins from the hulls and see how the yield of furfural according to Tollens was changed, also to obtain xylose from the hulls by means of acid hydrolysis, determine the yield of xylose according to Tollens, and then determine the pentosans remaining in the hulls.

For the removal of tannins the hulls were heated with distilled water in an autoclave for 2 hours under 1.5 atmospheres' pressure. During the heating the hulls lost 8.9 per cent of their dry weight. An analysis of the water extract obtained and of water-extracted hulls was made (Tables II and III). Tannins were determined according to the official standard method with powdered leather, sugar according to Bertrand, pentosans or xylose according to Tollens, cellulose according to Cross and Bevan, and lignin according to König (with 72 per cent sulfuric acid).

Table II. Analysis of Water Extract

Determination	Per Cent of Weight of Initial Dry Hulls
Loss in weight of hulls when first boiled in water	8.90
Solid residue of water extract	7.11
Tannins in water extract	6.92
Sugars according to Bertrand	0.24

The authors' assumption about the influence of tannins on the yield of furfural when determined according to Tollens is confirmed by the experiment. During the extraction with water nearly all the tannins are removed from the hulls. And 21.42 per cent of pentosans, when determined according to Tollens, is found remaining in the extracted hulls. If computed to the weight of hulls before treatment with water, 19.51 per cent is found. In determining pentosans in the original hulls, the method of Tollens did not detect 7.49 per cent of pentosans (19.51 − 12.02), which is of course a defect of the method. After water extraction, the hulls were exposed to a second heating for 2 hours in an autoclave with 4 per cent sulfuric acid solution at 2 atmospheres' pressure. During that time hydrolysis of pentosans to xylose took place. The acid extract, as well as hulls obtained after the second heating with acid, were again analyzed (Tables IV and V). Table IV shows that the acid extract contains 22.47 per cent of pentosans compared to the weight of hulls used, or 20.47 per cent compared to the weight of hulls before heating in water and acids. Moreover, 1.81 per cent of the initial weight remains in the hulls after both extractions.

Table III. Analysis of Hulls after Water Extraction

Determination	Per Cent of Bone-Dry Hulls: Before water extraction	After water extraction
Pure cellulose (free from pentosans)	46.63	51.25
Pentosans according to Tollens	19.51	21.42
Methyl pentosans	Traces	Traces
Lignin	17.50	19.21
Ash	0.76	0.83

Thus the experiments for obtaining xylose directly from cottonseed hulls show their pentosan contents to be 20.47 + 1.81 = 22.28 per cent. This is considerably more than the 12.02 per cent as determined in the initial hulls (Table I), and also more than the 19.51 per cent found in hulls extracted with water. It is obvious that the lower results of the two latter determinations are due to the influence on furfural of hull components extraneous to pentosans—in the first case the influence of the tannins and in the second possibly also that of the lignin of hulls.

Estimating the pentosan content to be 22.28 per cent, this yield can by no means be considered as the highest possible, because the authors have not determined the pentosans that passed into the water extract with the tannins. Moreover, when the residue of hulls was analyzed after the second boiling with acid, the possibility of the influence of lignin on the yield of furfural when pentosans are determined is not excluded.

Table IV. Analysis of Acid Extract

Determination	Weight of Dry Hulls: Before water extraction	Before acid extraction
	%	%
Loss in weight of hulls in second boiling	33.19	...
Loss in weight of hulls in first and second boilings	42.09	...
Sugars in boiling liquid, according to Bertrand	...	26.30
Pentosans in acid extract, according to Tollens	20.47	22.47

Table V. Analysis of Hulls after Extraction with 4 Per Cent Sulfuric Acid

Determination	Dry Hulls: Before water extraction	After acid extraction
	%	%
Pure cellulose (free from pentosans)	40.39	69.75
Pentosans according to Tollens	1.81	3.02
Methyl pentosans	Traces	Traces
Lignin	12.63	21.81
Ash	0.072	0.133

In further experiments it was decided to use samples of hulls obtained from mills at various ages and also samples of burrs, the so-called Chingalak, and to determine more accurately the influence of lignin on the yield of furfural when pentosans are determined according to Tollens. For this purpose samples were prepared of hulls and burrs from which tannins were partly removed and then, by further treatment, lignin was removed by chlorination. Chlorolignin is removed from the hulls by treatment with a 3 pe

Table VI. Determination of Pentosans in Hulls and Burrs

Expt.	Material for Determining Pentosan Content	Loss in Weight during Preliminary Treatment	Yield of Furfural: To bone-dry substance	Yield of Furfural: To bone-dry substance before treatment	Changes of Furfural Yield to Substance before Treatment
		%	%	%	%
1	Mill hulls (fresh)	...	13.345	....	.....
2	Same hulls after water extraction (100° C.)	7.05	15.485	14.392	+4.047
3	Same hulls after water extraction and chlorination	26.25	14.657	10.754	−2.591
4	Same hulls after water extraction and first and second chlorinations	38.99	13.159	7.937	−5.348
5	Ginnery burrs	...	7.726	....	.....
6	Same burrs after water extraction	35.06	10.584	7.318	−0.408
7	Same burrs after water extraction and chlorination	52.29	11.734	5.876	−1.850

cent solution of sodium sulfite. It is probable that part of the pentosans are removed at the same time, which makes it exceedingly difficult to show experimentally the influence of lignin on the yield of furfural.

In Table VI results of the determination of pentosans in hulls and burrs after various treatments are shown, as well as losses in weight because of these treatments.

Experiment 2 shows that here, also, the removal of tannins from the hulls resulted in an increase of 1.047 per cent of furfural yield as compared to the yield from hulls before extraction. This increase is in accordance with the increase of 1.789 per cent of the weight of initial hulls in the determination of pentosan content. The error in determination is equal to

$$\frac{1.789 \times 100}{22.76} = 7.86\%$$

where the denominator 22.76 is the amount of pentosans corresponding to the furfural content in experiment 1 (13.345 per cent). This quantity of furfural was held by the tannins of the hulls during the distillation of furfural according to Tollens. Here the increase in furfural yield after treatment with water is not so large as it was for hulls in the first determination. This is no doubt due to the difference in the properties of the hulls (those stored for a long time and those which are fresh).

Experiments 3 and 4 (Table VI) show that pentosans are very firmly combined with the cellulose of the hulls and the greater part is not removed even by repeated chlorination. When yields are compared to the initial weight of hulls used for treatment, the increase in yield of furfural in hulls is not shown. Apparently a large part of the pentosans, not considered by the authors quantitatively, disappears from the hulls during chlorination and sulfite treatment. Thus the attempt to prove by experiment the influence of lignin on the yield of furfural remains unsuccessful.

From experiments 6 to 7 it is evident that treatment of burrs with water does not result in an increase of furfural yield. Inasmuch as the water extract of burrs always contains substances which supply furfural, when heated with acid, the influence of burr tannins on the furfural yield is also apparent. Substances forming furfural in burrs are different from those in cottonseed hulls, since in the case of burrs some components of pectin substances play a considerable part. The water extract prepared for chemical analysis contained 2.097 per cent of pentosans compared to the weight of burrs, which corresponds to the theoretical yield of 1.23 per cent of furfural. If we add 1.23 per cent of furfural from substances passed into the water extract to the yield of furfural calculated on the weight of initial burrs (experiment 6 in Table VI), or 7.318 per cent, we shall have 1.23 + 7.318 = 8.548 per cent of furfural from burrs after water extraction. The difference—8.548 − 7.415 = 1.133 per cent of furfural, or 1.93 per cent of pentosans when its yield is determined from untreated burrs—is obviously concealed during the determination on account of the influence of tannins. The error of the determination is

$$\frac{1.133 \times 100}{7.415} = 15.2\%$$

Table VII shows results of further experiments which were carried out on materials of different age before and after a slight treatment with water. These experiments were made to determine how the content of pentosans and other compounds capable of reducing furfural changed with variation in the age of the raw material, and to verify the influence of tannins on the process of determining pentosans.

Table VII. Experiments with Materials of Different Ages

Expt.	Material for Determination of Pentosans	Loss in Weight of Material Treated with Water	Yield of Furfural to Dry Substance	Before Treatment: Furfural yield calculated to weight of dry substance	Changes of furfural yield to substance
		%	%	%	%
10	Mill hulls (sample 3) fresh	....	14.442	....	.....
11	Same hulls after treatment with water	6.325	16.170	15.147	+0.705
12	Mill hulls (sample 4) with moldy odor	....	14.408	....	.....
13	Same hulls after treatment with water	6.255	15.758	14.769	+0.361
14	Hulls from seeds 35 days old	....	13.395	....	.....
15	Same hulls after treatment with water	21.452	17.690	13.895	+0.500
16	Hulls from seed 60 days old	....	12.010	....	.....
17	Same hulls after treatment with water	14.899	14.656	12.472	+0.462
18	Hulls from seed 80 days old	....	12.181	....	.....
19	Same hulls after treatment with water	4.314	12.754	12.204	+0.023
20	Burrs from opened bolls	....	10.658	....	.....
21	Same burrs after treatment with water	25.814	13.627	10.110	−0.548
22	Burrs from bolls 20 to 30 days old	....	9.991	....	.....
23	Same burrs after treatment with water	28.530	12.430	8.883	−0.008

As seen from experiments 11, 13, 15, 17, and 19, treatment of all the samples of hulls with water resulted in an increase of furfural yield. Using the calculation for initial substance (before treatment with water) we have an increase of furfural yield from 0.023 for collected hulls and 0.705 per cent for mill hulls (or 0.039 and 1.21 per cent pentosans).

For samples of hulls 35 days old this increase is larger than for hulls from ripe seeds. This is in full conformity with the known fact that, with increased age of seeds the tannin content is diminished and its character is changed. While the tannins of unripe seeds readily pass into a water extract,

forming a colorless solution, for the most part tannins from ripe seeds are converted into more complicated compounds (lignin), and the remaining tannins become colored substances with a phlobaphene character, passing with more difficulty into the water extract than the tannins of hulls from unripe seeds.

Burrs (experiments 21 and 23) did not show any increase in furfural yield over their weight before treatment with water, but taking into consideration that a considerable part of the substances apt to form furfural have passed into the water extract one has to admit the influence of tannins on the yield of furfural here.

Where tannins are present in a substance to be examined, it is necessary to consider the possibility of decrease in yield of furfural, and hence a decrease in pentosan content, determined according to Tollens. The influence of tannins is shown by experiments to determine furfural yield from a sample after removing tannin extract with water and comparing the furfural yield to the weight of substance before extraction. If there is an increase in furfural yield after removal of tannins their influence on the determination of pentosans according to Tollens becomes apparent. If the yield of furfural is lower after extraction with water, it is possible that substances forming furfural (as with burrs) belong to the group of substances readily soluble in water. In this case it would prove useful to determine the furfural yield from a water extract after precipitating the tannins.

The determination of pentosans according to Tollens is quite insufficient for accurate work with substances containing tannins (and perhaps also lignin) and must be supplemented by the extraction of tannins from the substance and by direct hydrolysis of pentosans to xylose. The pentosan content (furfural-forming substances in general) is to be determined as a total of three determinations—in water extract (after precipitation of tannins), in acid extract, and in the residue after hydrolysis with acid.

The influence of lignin on the determination of pentosans according to Tollens can as yet be only supposition, but at the first opportunity the authors plan to investigate by experiment the existence of such an influence. The importance of tannins in the determination of pentosan content is of greater influence than all the other known errors of the Tollens method; it leads to lowered results, whereas the other defects of the method give exaggerated results.

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Filtering Fruit Juices and Plant Extracts

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The large-scale laboratory filtration of fruit juices and aqueous extracts of plant material is often a very troublesome operation when suction flasks and Büchner funnels only are to be used. Some years ago the authors in the Research Laboratory of the California Fruit Growers Exchange developed a method for orange juice that has since been successfully applied in many instances. In effect, the operation combines ordinary laboratory suction filtration with the principles of industrial filtration. The filter is prepared as follows:

A piece of filter cloth if available, or a fairly heavy piece of muslin, is cut to fit loosely into the bottom of a Büchner funnel of suitable size. A slurry of paper pulp of a type commercially available for filter mass is prepared in water. A thin layer of the pulp slurry is poured onto the filter and distributed evenly, and then suction is applied to drain the mass thoroughly, care being taken, however, that the pulp does not become compressed too tightly. Now a dilute suspension of a commercial filter aid, such as Filter-Cel, is prepared and, without disturbing the pulp mat, a thin layer of the diatomaceous earth is allowed to spread out on the pulp. Moderate suction is then applied to pull this down on the pulp. These operations may be repeated several times, building up alternate layers of pulp and filter aid until the funnel is about half full, if a large quantity of liquid is to be filtered.

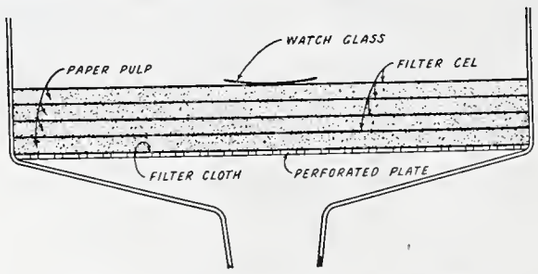

Figure 1. Cross Section of Filter

There are two objects of the alternate layers of paper pulp and filter aid. Extremely fine particles are easily retained by the filter, so that brilliantly clear filtrates result. By using and removing successively the paper-pulp filter mats, a large quantity of liquid may be filtered with the minimum of dilution or loss in starting the filtering operation.

Filtration

The liquid to be filtered is agitated with an amount of filter aid appropriate to the material. About 250 cc. were found sufficient for a liter of orange juice. In pouring the mixture of liquid and filter aid onto the filter, care must be taken not to disturb the mat. It is advisable to place a small watch glass in the center and to pour upon it. Filtration is begun with only as much vacuum as is required to maintain a flow through the mat. Suction is increased gradually as the mat clogs.

A cake of diatomaceous earth will build up in the funnel. When this becomes too thick for convenience, the filter may be sucked fairly dry without raising the vacuum, and, with suction off, the built-up cake and the top layer of pulp may be removed from the next thin layer of filter aid. Filtration may be continued as before.

Operating in this manner, the authors were able to filter with an 8-inch (20-cm.) Büchner funnel as much as 20 liters of orange juice through one prepared filter mass at a rate of about 15 liters per hour. The method has since been applied to a variety of products, such as pectin solutions and tannin extracts, without difficulty.

Various grades of natural and calcined diatomaceous earth filter aids are available. The use of higher grades of material may be desirable in some cases.

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Determination of Small Quantities of Sodium Carbonate

Warder's Method with Improved Technic

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For the determination of sodium carbonate in commercial caustic soda, there is no satisfactory direct volumetric method, and usually a determination of carbon dioxide is resorted to (*5*). Winkler's method yields higher results, owing to the precipitation of barium silicate (*3*, *4*), and to the precipitation of basic barium carbonate (*6*), when carried out according to the usual procedure.

Theoretically Warder's (*8*) method is suitable for mixtures containing much hydroxide and little carbonate (*2*), like commercial caustic soda, but the usual procedure is far from precise. Slight errors in the two end points affect the result seriously. If 45 cc. of a standard acid are used for the complete titration and an error of 0.04 cc. is made at each end point, the result for carbonate would be affected by 0.36 per cent when the errors are cumulative in nature.

Han and Chao (*1*) have devised a procedure for precisely measuring the difference between the two end points and have used it for determining the carbonate content of volumetric sodium hydroxide solutions. The result checked within 0.02 per cent against the gravimetric evolution method. This procedure, however, is not suitable for caustic soda that contains an appreciable quantity of acid-consuming impurities.

Impurities that might occur in appreciable quantities in commercial caustic soda are sodium silicate, sodium aluminate, iron, lime, and magnesia. Sodium silicate behaves like sodium hydroxide during the titration and offers no interference in the carbonate determination. Sodium aluminate is decomposed with the separation of aluminum hydroxide at the first end point (*7*). Aluminum hydroxide as well as ferric hydroxide, lime, and magnesia consume part of the acid for the second end point and, when present in appreciable quantities, cause a positive error in the carbonate determination.

The author has recently further modified the procedure. The error due to acid-consuming impurities was prevented by filtering the solution after reaching the first end point, but before adding any acid for the second end point. From the data obtained not only the quantity of sodium carbonate can be accurately calculated, but also that of sodium hydroxide. Although carbon dioxide determination yields accurate results for sodium carbonate, yet the sodium hydroxide content of the sample when calculated from total alkali and carbonate is slightly high unless due correction is made for the acid-consuming impurities present. Certain details of Han and Chao's procedure have also been simplified so that it can be more conveniently used for commercial work.

Procedure

The procedure differed from that of Han and Chao (*1*) in the following points:

1. No carbon dioxide–free air was used for sweeping the Erlenmeyer flask during all titrations.
2. The long nozzle of the buret for N hydrochloric acid was inserted into a two-holed rubber stopper, the other hole of which carried a soda-lime guard tube.
3. Instead of 0.01 N solutions, 0.02 N hydrochloric acid and 0.02 N sodium hydroxide were used for the precise measurement of the difference between the two end points. During the addition of 0.02 N solutions, the Erlenmeyer flask was not protected from atmospheric carbon dioxide, but the titration was quickly performed.
4. The solution was filtered through a 9-cm. filter and washed with 35 cc. of ordinary distilled water if appreciably turbid at the first end point.

Discussion

Table I gives typical results expressed in per cent of sodium carbonate calculated on the weight of the solid sample. The results were slightly higher than the gravimetric method, but close agreement was obtained by applying a correction of −0.03. The procedure has been successfully used in summer as well as in winter, with room temperatures ranging from 10° to 31° C. With samples high in carbonate and iron content, the location of the first end point was somewhat difficult. In such an event, the titration was continued until the pinkish tint of the indicator was completely discharged.

Table I. Comparison of Gravimetric and Volumetric Methods

Sample, Weight in 3450 cc. of Solution[a]	Gravimetric Determinations		Volumetric Determinations, Not Filtered 0.02066N		Volumetric Determinations, Filtered 0.02066N	
	CO_2	Na_2CO_3	HCl[b]	Na_2CO_3[c]	HCl[b]	Na_2CO_3[c]
	Gram	%	*Cc.*	%	*Cc.*	%
Lime Process, A	0.0521	0.61	5.49	0.62	5.48	0.62
Bottom of	0.0520	0.61	5.55	0.63	5.54	0.62
drum	0.0520	0.61	5.38	0.61	5.48	0.62
142.18 grams		(0.61)		(0.62)		(0.62)
Lime Process, B	0.0698	0.80	7.64	0.85	7.21	0.80
Bottom of	0.0699	0.80	7.52	0.84	7.20	0.80
drum	0.0705	0.81	7.37	0.82	7.18	0.80
145.44 grams		(0.80)		(0.84)		(0.80)
Electrolytic	0.0852	1.02	8.56	1.00		
Av. sample	0.0845	1.01	8.69	1.02		
139.31 grams	0.0844	1.01	8.77	1.03		
		(1.01)		(1.02)		
Löwig Process	0.1269	1.43	12.63	1.41		
Top of drum	0.1267	1.43	12.87	1.43		
147.49 grams	0.1265	1.43	12.64	1.41		
		(1.43)		(1.42)		
Löwig Process	0.1132	1.32	11.45	1.32		
Middle of	0.1124	1.31	11.54	1.33		
drum	0.1130	1.32	11.61	1.34		
142.58 grams		(1.32)		(1.33)		
Löwig Process	0.1682	1.93	17.25	1.97	16.80	1.92
Bottom of	0.1678	1.93	17.83	2.04	17.10	1.95
drum	0.1673	1.92	17.32	1.98	17.05	1.95
144.62 grams		(1.93)		(2.00)		(1.94)

[a] For gravimetric determination 500 cc. and for volumetric determination 45 cc. of solution were used.
[b] Volume used for the second end point.
[c] A correction of −0.03 has been applied.

With extremely impure caustic, the sample solution can be allowed to settle and a clear portion used for the titration. Any aluminum hydroxide formed at the first end point is removed by filtration. The boiling can be omitted if methyl orange or bromophenol blue is used as indicator for the second end point. The color change, however, is not sharp with 0.02 N acid.

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Quantitative Determination of Coumarin in Plant Material

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COUMARIN is widespread in the plant kingdom. In certain species of forage plants it is present in sufficient quantity to impart a disagreeable taste, disliked by farm animals. An investigation of the coumarin content of various strains of sweet clover developed by the Department of Agronomy at the West Virginia Agricultural Experiment Station necessitated the quantitative determination of this substance. Methods for the determination of coumarin in vanilla extract are not well suited to the removal and determination of coumarin in plant tissues, and a search of the literature showed only the method of Obermayer (*2*) available for this purpose.

Experimental

In Obermayer's method, 10 grams of air-dry sweet clover meal are extracted with ether, the extract is transferred to a 500-cc. distilling flask, and the ether evaporated at room temperature. After removal of the ether, 300 cc. of a 25 per cent solution of calcium chloride are added and the coumarin is distilled from this solution. The temperature at the end of the distillation should be 179° to 180° C. An aliquot part of the distillate is then titrated with 0.1 *N* potassium permanganate in a special manner described by the author.

Since the method does not state how long the extraction with ether should be continued, the first problem was to determine the extraction period necessary for the complete removal of the coumarin. To accomplish this a battery of ten Soxhlet extractors was set up and duplicate determinations were run on five varying periods of extraction of the same material. Ten-gram samples of sweet clover were extracted for periods of 24, 30, 37, 49, and 72 hours, respectively.

The results showed that the titration value of the sample increased up to 30 hours of extraction, after which it decreased. Just why extracting 37 to 72 hours gave lower results than 30 hours was not clear. However, it was thought that the long-continued heating of the extract in the receiving flask might affect its titration value. Next a series of samples were extracted in quadruplicate for periods of 2, 4, 8, and 12 hours, the receiving flask being replaced by a new flask at the end of each period. This made a total of 26 hours' extraction.

Titration of 100-ml. aliquots of the distillates at the end of 2 hours and after an additional 4, 8, and 12 hours of extraction required 18.99, 8.34, 7.66, and 6.81 ml. of 0.1 *N* potassium permanganate, respectively, or a total of 41.80 ml. for the total 26 hours. These values are the mean of four distillations. Since the titration value for the final extraction period was so large (6.81 ml.), the extractions were continued for additional periods of 24, 40, and 20 hours. The mean titration values for 100-ml. aliquots of these extracts were 5.50, 4.78, and 4.00 ml. of 0.1 *N* potassium permanganate, respectively, or a grand total of 56.08 ml. for 110 hours.

These values are considerably higher than those secured from continuous extraction over similar periods without change of receiving flasks, indicating that long-continued heating of the ether extract in the receiving flask does reduce the titration value. The final 20-hour extract gave a relatively high titration and a positive Wichmann-Dean (*1*) test for coumarin, indicating that the coumarin is not completely removed even after 90 hours of extraction.

Three additional series, in which 5-gram samples of the same material were employed, were extracted in triplicate by varying periods for a total of 26 hours. The extracts were combined and the composite extract was distilled and titrated as before. The samples were then subjected to further extraction for periods of 70 and 24 hours.

In series 1 the flasks were replaced at intervals of 2, 5, 7, and 12 hours, and the 100-ml. aliquot required 20.87 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 4.16 and 0.82 ml., respectively, or a total of 25.85 ml. for 120 hours.

In series 2 the flasks were replaced at intervals of 4, 9, and 13 hours, and the 100-ml. aliquot required 17.73 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 3.95 and 0.94 ml., respectively, or a total of 22.62 ml. for 120 hours.

In series 3 the sample was extracted continuously for 26 hours without replacement of the receiving flask, and the 100-ml. aliquot required 14.25 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 3.62 and 0.95 ml., respectively, or a total of 18.82 ml. for 120 hours.

Examination of the values for the 26-hour extraction periods in series 1, 2, and 3 shows beyond question that the longer the sample is extracted before the flask is replaced, the lower the titration secured. In addition to this disturbing factor of loss on continued extraction the difficulty of complete removal of coumarin is a serious problem. The final 24-hour extraction period in all three series gave a positive Wichmann-Dean (*1*) test for coumarin but required 1 ml. or less of the potassium permanganate solution for titration, indicating that 120 hours of extraction is sufficient, although impractical, for its complete removal. Results secured from more finely ground material, to pass a 0.5-mm. sieve, were almost identical with those previously given.

Extraction by Steam Distillation

Since the ether-extraction method for removing coumarin from the sweet clover samples was found both difficult and variable as to results, some other method for its removal was sought. Inasmuch as coumarin is known to be volatile with steam, the possibility of its removal from the samples by steam distillation under reduced pressure was considered.

The procedure described below was finally adopted, although various modifications were tried as successive steps in the development of the method seemed to warrant.

A 5-gram sample ground to pass a 1-mm. sieve is placed in a 1-liter, long-neck, round-bottom Pyrex flask, and 80 cc. of water are added and mixed with the sample. The flask is fitted with a 2-hole rubber stopper carrying a Kjeldahl distillation bulb and a steam inlet tube which extends to the bottom of the flask. The distilling flask is joined through the connecting bulb to a 25-inch (63-cm.) Allihn condenser and the flask immersed in a boiling water bath. A 4-liter Pyrex beaker serves as a transparent bath through which the steam distillation can be observed and controlled. A 1-liter suction flask is fitted to the condenser to collect the distillate. The entire system is then connected to a water suction pump by rubber tubing attached to the side tube of the receiving flask. A mercury manometer is inserted in the line for measuring the pressure.

It is convenient to run the distillations in duplicate by attaching two sets of apparatus to the same steam jet and to the same suction pump. Screw clamps at suitable points in the line assist in controlling the rate at which the steam is admitted and distributed to the flasks and the pressure reduced. A stream of dry steam is passed into the flasks for 1 to 2 minutes until the contents reach a vigorous boil and the distillate begins to drip

from the condenser. At this time the pressure is reduced as rapidly as possible but at such a rate as to prevent boiling over, until the pressure in the system is 140 mm. of mercury. The distillation is continued at 140 mm. until the flasks are dry, after which they are disconnected and removed from the water baths. The connecting bulb, steam inlet tube, and inside of the distilling flask are rinsed down with an additional 80 cc. of water and the contents redistilled as before.

This procedure is repeated until six distillations have been made, after which the condenser is rinsed down into the receiving flask and the distillate transferred to a 1-liter volumetric flask. The flask is made up to volume, and 50-ml. aliquots of distillate are treated with 4-ml. of 0.25 *M* lead acetate, stirred, covered, and allowed to stand several hours or overnight. The excess lead is then precipitated by adding 0.17 *M* disodium phosphate in a quantity just equivalent to the 4-ml. of lead acetate used (this amount having been determined previously by titration) plus 0.5 ml. additional. The precipitate of lead phosphate is allowed to settle for 30 minutes and 25 ml. of zinc sulfate solution,[1] made by dissolving 200 grams of zinc sulfate in 1 liter of water, are added and mixed. The whole is permitted to stand at least 4 hours, after which the combined precipitates of lead tannate, lead phosphate, and zinc phosphate are removed by centrifugalizing in a 100-cc. centrifuge tube. The supernatant liquid is poured off into a 500-cc. Erlenmeyer flask, the precipitate washed twice with 25 cc. of water, and the washings are combined with the original decantation. This solution is then titrated indirectly with 0.1 *N* potassium permanganate according to the method of Obermayer (*2*) as follows:

A measured quantity of potassium permanganate solution is added in excess (usually 25 ml.), the total volume diluted to approximately 150 cc., and heated on an asbestos board for 10 minutes. The hot solution is filtered through an asbestos mat in a Gooch crucible, the mat washed, and the excess permanganate decomposed with a known amount of 0.1 *N* oxalic acid solution added in excess. The resulting solution is acidified immediately with 25 cc. of 2 *N* sulfuric acid and the excess oxalic acid titrated with 0.1 *N* potassium permanganate, during which the temperature is maintained at 70° to 80° C.

The permanganate titration accounts for only about 93 per cent of the total coumarin where pure coumarin is used, which necessitates the use of a titration factor. Blank titration values on reagents should be subtracted from the total titration values. The equation for the reaction as qualified may be written as follows:

$$3C_9H_6O_2 + 38KMnO_4 \longrightarrow 38MnO_2 + 19K_2O + 27CO_2 + 9H_2O$$

Preliminary Trials

Preliminary work indicated that steam distillation might be utilized for the removal of coumarin. It soon became apparent that several distillations were necessary to remove the coumarin completely from a given sample and that in this procedure a small but unknown quantity of noncoumarin reducing material was carried over into the distillate along with the coumarin. Since it was desired to determine the coumarin removed by titration with 0.1 *N* potassium permanganate, the presence of reducing substances other than coumarin presented a serious objection to the proposed method unless these substances could be either eliminated or evaluated in satisfactory manner and proper correction made.

In a typical preliminary trial, duplicate 5-gram samples were distilled four times, and each distillate was made up to 500 ml. A 30-minute period of distillation at atmospheric pressure was carried on before the pressure in the system was reduced and 60 cc. of water were added instead of 80 as in the final method. Fifty-milliliter aliquots from each of the four distillates required 10.50, 4.05, 1.75, and 0.51 ml. of 0.1 *N* potassium permanganate, respectively, or a total of 16.81 ml. for the four distillations. Wichmann-Dean tests for coumarin in the distillates indicated that most of the permanganate requirement was due to coumarin.

The next factor to receive consideration was the effect of using different degrees of reduced pressure, and consequently different temperatures, in the distillation flasks. Thermometers were placed in the distillation flasks and a mercury manometer was inserted in the line. Three different degrees of temperature and pressure were tried with 5-gram samples in duplicate and the distillation procedure last described. The temperatures and pressures used and the mean values secured are shown in Table I.

Table I. Effect of Different Degrees of Temperature and Pressure on the Steam Distillation of Sweet Clover

Distillation Number	0.1 *N* $KMnO_4$ Required for 50 ml. of Distillate: 150 mm. of mercury and 60° C.	270 mm. of mercury and 73° C.	390 mm. of mercury and 82° C.
	Ml.	*Ml.*	*Ml.*
1	12.23	13.05	14.30
2	2.80	3.46	2.83
3	1.05	1.31	1.13
4	0.53	0.60	0.60
Total	16.61	18.42	18.86

The results show a considerable effect of temperature and pressure on the total titration value. The fourth distillation was uniformly low in each case, which may be taken to indicate that most of the coumarin is removed by four distillations. Qualitative tests for coumarin on equal volumes of distillates from the lowest and highest temperatures tried showed that the distillates from the 60° distillation contained as much coumarin as those from the 82° distillation and indicated a greater removal of noncoumarin reducing material at the higher temperatures and pressures. This point was confirmed by direct test for tannin derivatives.

It seemed desirable also to secure additional data on the effect of time of distilling at atmospheric pressure, before reducing the pressure for distillation to dryness.

Consequently quadruplicate sets of four distillations each were carried out, the time of distillation at atmospheric pressure being varied from 5 to 30 minutes. The reduced pressure used was 140 mm. of mercury, which gave a distillation temperature of 59° C. Pressures lower than 140 mm. were tried but were found to be less satisfactory in manipulation. Five-gram samples were used, the distillates made up to 500 ml., and 50-ml. aliquots were titrated. Total titration values secured by adding the values for each set of four distillations are given. The 5-, 10-, 15-, 20-, and 30-minute distillation periods required 14.24, 14.63, 14.82, 15.05, and 15.28 ml. of 0.1 *N* potassium permanganate, respectively, these values being the mean of four determinations.

The results show somewhat higher values for the longer periods of heating; qualitative tests for noncoumarin reducing substances in the first distillates in each set also indicated a higher content of this material in the distillates from the longer periods of heating. Determinations of the vapor pressure curve for coumarin above and below its melting point in the range of the distillation temperatures being employed gave unexpected results, and the question arose as to whether the preliminary period of distillation at atmospheric pressure might not be dispensed with entirely. Several trial runs showed that this could be done to advantage, in that the quantity of noncoumarin reducing substances was diminished and the time required to complete a distillation was shortened without affecting the removal of coumarin. The effect of maintaining the water bath at 63° to 66° C. was also tried, but the lower temperature required a longer period for distillation, which again resulted in an increased quantity of noncoumarin material.

For these reasons the procedure was modified in that 80 cc. of water were added instead of the 60 cc. originally used, and as soon as the contents of the flask reached a rolling boil, usually requiring 1 to 2 minutes, the pressure was reduced. The time required to reduce the pressure in the distillation flask to 140 mm. of mercury was 3 to 4 minutes, and the total period of distillation about 8 minutes for each 80-cc. portion

[1] The number of milliliters of zinc sulfate solution used should be the same as that of the 0.1 *N* potassium permanganate added in the next step. If less than 25 ml. of potassium permanganate are added the zinc sulfate may be correspondingly reduced.

of water added. It was found also that moderate variations in the amount of water added (75 to 100 cc.), in the reduced pressure utilized (135 to 145 mm.), and in the fineness of the sample (passing a 0.5 to 1 mm. sieve), were without appreciable effect upon the results secured.

Noncoumarin Reducing Substances

Prior to this time, efforts had been made to learn the general nature of the compounds other than coumarin affecting the permanganate titration. Behavior toward Fehling's solution and ferric chloride, qualitative tests for lignin, saponins, formaldehyde, and tannins and their derivatives had been run on numerous distillates. Of the various tests made, only that for pyrogallol and related substances, resulting in a brownish precipitate with Nessler's reagent, was positive. Dilute solutions of pure pyrogallol and Nessler's reagent gave a test very similar to the test obtained with sweet clover distillates and Nessler's reagent.

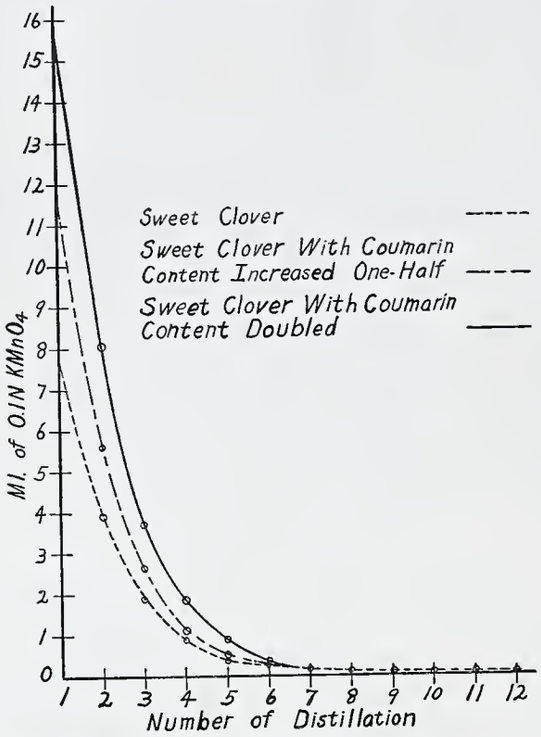

Figure 1. Distillation Curves for Sweet Clover Alone and Reënforced with Pure Coumarin

In order to ascertain the effect of steam distillation on material of high tannin content, a 5-gram sample of tea was distilled four times and each distillate made up to 500 ml. Fifty-milliliter aliquots required 0.30, 0.20, 0.17, and 0.10 ml. of 0.1 N potassium permanganate, respectively. Even though tea is high in tannins, only relatively small amounts are removed by the steam-distillation method.

Further information was now desired relative to the behavior of samples of varying coumarin content under steam distillation. Accordingly, sweet clover samples having a high and a low coumarin content were distilled over and over until the distillates gave little or no permanganate titration. Along with these samples, similar samples were reinforced with varying amounts of a solution of pure coumarin, and distilled repeatedly. The amounts of coumarin added were of sufficient quantity to increase that naturally present by approximately 50 and 100 per cent, respectively. The titration values of a representative sample with and without added coumarin are shown graphically in Figure 1. The points on the curves are all means of four determinations.

Irrespective of their coumarin content, the samples behave similarly under steam distillation. They also show essentially equal titration values for the seventh distillation. It appears clear, therefore, that all the coumarin is removed from the sample in six distillations and that the titration values beyond the sixth are due to noncoumarin reducing substances. The test for tannin materials and also that for coumarin support this view. It was not possible to secure a Wichmann-Dean test for coumarin beyond the fifth distillate.

In an effort to eliminate the noncoumarin material distilled over during the removal of coumarin, samples of sweet clover were distilled repeatedly and the distillates treated with a solution of neutral lead acetate. The distillates always gave a distinct precipitate with lead acetate additions, and the deleaded solutions gave lower titration values than the untreated distillates. Further, solutions of pure coumarin when treated with lead acetate gave quantitative values for the coumarin added, showing it to be unaffected by the treatment. Somewhat contrary to expectation, trials with sweet clover distillates showed that it is immaterial whether the precipitates of lead tannate, lead phosphate, and zinc phosphate are removed separately, or all together, provided time for complete precipitation is allowed in each case. Filtration through asbestos mats on Gooch crucibles can be substituted for centrifugalizing with equally good results. The centrifuge method is preferred because it is more rapid and convenient.

In a typical example showing the effect of treatment with lead acetate, duplicate 5-gram samples were distilled eight times and the distillates made up to 500 ml. Fifty-milliliter aliquots were taken for direct titration and for titration after treatment with lead acetate. When titrated directly the eight aliquots required 6.60, 3.16, 1.54, 0.70, 0.44, 0.39, 0.16, and 0.12 ml. of 0.1 N potassium permanganate, respectively. After leading and deleading the corresponding requirements were 6.46, 3.08, 1.37, 0.54, 0.31, 0.22, 0.02, and −0.01 ml., respectively. The two series differ by an almost constant amount and the potassium permanganate requirement of the treated distillates approximates zero for the seventh and eighth distillations.

Plant materials containing only small amounts of coumarin and considerable amounts of volatile reducing substances not precipitated by lead acetate could not be determined accurately by this method. However, it has been applied to soy-bean hay, cowpea hay, alfalfa hay, tonka beans, privet leaves, and other plant tissues in less extensive trials than with sweet clover but with satisfactory results.

Approximate Method for Comparative Purposes

Although six distillations are required to remove all the coumarin from a sample of sweet clover, nevertheless a close approximation to this value may be secured by discontinuing the distillations at the end of the fourth and omitting the lead acetate treatment of the distillates. About 95 per cent of the total coumarin present in the sample is removed in the first four distillations. On the other hand, when calculated as coumarin the noncoumarin reducing material in these same four distillations varies from 3 to 5 per cent. By this procedure the small amount of coumarin left in the sample is approximately equal to, and offset by, the noncoumarin titratable material which distills over.

This shorter method has been shown to be sufficiently accurate for sorting different strains of sweet clover of varying coumarin content and is being utilized for that purpose in this laboratory. It greatly reduces the amount of time and labor required where large numbers of samples are handled. Where greater accuracy is desired, the longer procedure, involving a larger number of distillations and treatment with lead acetate, is used.

Summary

The steam distillation method for removing coumarin from plant tissues has certain decided advantages over the ether extraction method. It gives excellent results with sweet clover and seems to apply successfully to other species also. For comparative purposes where a high degree of accuracy is unnecessary, the number of distillations may be reduced and the distillates titrated directly without further treatment. For more accurate results the number of distillations is increased, and the noncoumarin reducing substances are removed by precipitation with lead acetate.

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Determination of Bromide in the Presence of Large Excess of Chloride

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During a study of the metabolism of brominated compounds, a number of the methods previously reported for the determination of bromides in the presence of large excess of chlorides proved unsatisfactory. Most of them depend upon the oxidation of the bromide to bromine under conditions so regulated as to avoid the simultaneous production of chlorine. When the concentration of bromide is small and that of chloride is high, this is impossible; to overcome this difficulty the bromine first obtained is frequently converted to bromide and is then reoxidized in a similar manner. In some processes even a third oxidation is used. Usually the bromine finally obtained is determined iodometrically. Each oxidation introduces the possibility of loss of bromine, and if any chlorine is carried over in the last oxidation it will be reported as bromine. The procedure of Behr, Palmer, and Clark (*1*) gave the most satisfactory results, but even with very careful manipulation it was accurate to only about 2 per cent. Since this was not sufficient for the authors' purposes, the following procedure was worked out: The bromine is liberated by means of moderate excess of chlorine water, collected in sodium sulfite solution, and titrated potentiometrically in sulfuric acid solution with potassium bromate. This procedure has been satisfactorily used by one of the authors in collaboration with R. C. Corley for the analysis of about fifty urine samples in a study of the excretion of bromides following the ingestion of brominated compounds.

Materials and Apparatus

Potassium bromide for use in making known solutions had to be synthesized, since the best obtainable potassium bromide contained "not more than 0.75 per cent potassium chloride." Bromine was freed of chlorine by shaking with three successive portions of aqueous sodium sulfite and separating. The purified bromine was then reduced by sulfur dioxide and water, and the resulting hydrobromic acid solution was redistilled until free of sulfuric acid, and neutralized with c. p. potassium hydroxide. The potassium bromide obtained in this manner was recrystallized twice and dried at about 110° C.

Chlorine water was made by absorbing in water the chlorine obtained by electrolysis of hydrochloric acid. To remove any traces of bromine from the hydrochloric acid, it was diluted to about constant boiling strength, treated with chlorine, and boiled. The strength of the chlorine water was checked iodometrically from two to three times a week.

The potassium bromate was a c. p. product recrystallized and dried at about 110° C.

Sulfuric acid, potassium hydroxide, copper sulfate, and sodium chloride of c. p. or reagent quality grade were used without further purification. The sodium chloride was found to contain 0.001 per cent of bromide. The chloride in the other chemicals was reported from 0.001 to 0.005 per cent, and undoubtedly the bromide was only a small fraction of this. With the exception of the chlorine water, all solutions were made by weighing the appropriate substance and making up to volume in calibrated volumetric flasks.

The apparatus for liberating the bromine from the solution of halides consisted of a 50-ml. flask with an inlet tube extending from top to bottom, and a delivery tube leading to an absorption train of two test tubes, illustrated in Figure 1. Suction is applied at *F*. *A*, *C*, and *D* are ungreased ground-glass joints. A rubber stopper was used at *E*, since the air passing it no longer contains bromine vapor. This apparatus was designed for samples not exceeding 25 ml. A larger flask would be desirable for larger samples, and if the bromine content is high, the absorption system should also be enlarged.

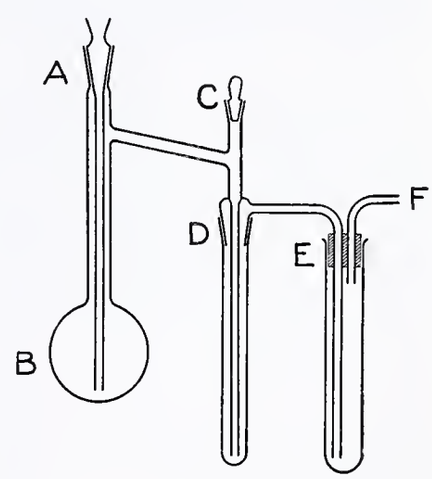

Figure 1. Apparatus for Liberating Bromine

A Leeds & Northrup student potentiometer with a portable, enclosed lamp and scale galvanometer was used to measure the potentials.

Procedure

The bromine in the sample to be analyzed should be present as bromide ion. For materials in which the bromine is in organic combination, or when organic material is mixed with the bromide, the ashing method of Behr, Palmer, and Clark (*1*) was found to be very satisfactory.

Sodium sulfite amounting to about 20 mg. plus three to five times the estimated weight of bromine in the sample is weighed out, dissolved in water, and put into the absorption tubes, with about 80 per cent of the sulfite in the first tube. The rapid oxidation of sulfite by air makes the large excess necessary. While a slow stream of air is sucked through the apparatus, the sample is introduced through the inlet tube, rinsed down, made acid with sulfuric acid, and chlorine water estimated to be in slight excess

of the bromine content is introduced. The flask is heated to about 100° C. for 10 to 15 minutes and cooled. Two or three further additions of chlorine water are made, heating the flask after each addition. Unless the bromine content is very small it is desirable to use a total of not more than three times the theoretical amount of chlorine water, and the later additions are made smaller than the first one unless the development of color on the second addition shows that the first was too small.

The air stream is then stopped, and the contents of the absorption tubes are rinsed into a small beaker suitable for the titration, made alkaline, and evaporated on a steam bath. A drop of 1 per cent copper sulfate is added before evaporation to catalyze the oxidation of the excess sulfite by air. After evaporation the sides of the beaker are rinsed down and the sample is again evaporated to insure the oxidation of all of the sulfite, made up to suitable volume with about 7.5 N sulfuric acid, and titrated potentiometrically with standard potassium bromate, using a platinum wire electrode as indicator, and a 0.1 N calomel electrode as reference. The solution is stirred by a small mechanically driven glass stirrer throughout the course of the titration. The titration vessel is surrounded by ice to minimize the loss of bromine.

Before addition of any bromate the potential is erratic and of no significance. The potential after the addition of a small quantity of potassium bromate (0.02 ml. was usually used) is a very useful indicator of sulfite; if sulfite is still present, the potential remains low, below 0.3 volt, but if it has been completely oxidized, the potential goes to 0.57 to 0.61 volt. The end point is taken as the point of maximum rate of change of potential with added potassium bromate. The authors have used Fenwick's (*3*) formula for calculating the end point. The end-point potential varies from case to case, from 0.78 to 0.83 volt, probably because of the variation in the concentration of dissolved bromine. When no bromide is initially present in the solution to be titrated, the end-point potential is exceeded upon the first addition of bromate.

Discussion

In order to test the reliability of the potentiometric titration of bromide in the presence of chloride, a series of titrations was carried out under various conditions, with the results shown in Table I. The ratio of chloride to bromide was kept small and the preliminary oxidation with chlorine water was omitted. Known quantities of chloride and of bromide were mixed, made alkaline and evaporated, made to suitable volume with sulfuric acid and titrated. Series 1 shows that if the concentration of chloride does not exceed two to three times the equivalent concentration of bromide present, the amount of bromate required is independent of the chloride content. With larger relative amounts of chloride the end point is not sharp and the results are high. For this reason a controlled amount of chlorine water is employed in the first oxidation.

Series 4 and 5 show that an increase in final volume, with corresponding decrease in acid concentration, decreases the amount of bromate used toward the stoichiometric value. With appropriate adjustment of acid concentration and of volume at the end point, the stoichiometric ratio of bromate to bromide may be obtained, but when the concentration of bromide is very small, such adjustment makes the titration very tedious, for under these conditions the potentials are slow to reach steady values. For this reason it is recommended that in the determination of small quantities of bromides, the volume of solution at the end point be kept small, the final acid concentration be from 6 N to 7 N, and that known samples be run under the same conditions and the corresponding correction factor be applied. In effect the bromate is standardized by the known bromide solution.

Table II gives some results of the complete procedure. From 0.3 to 1.0 gram of sodium chloride was added to the samples containing more than 1 mg. of bromide, and approximately 30 mg. of sodium chloride to those containing less than 1 mg. Very great excesses of sodium chloride were avoided to obviate large corrections for the bromide in the sodium chloride. There is no reason to believe that larger amounts of chloride would in any way interfere with the liberation of bromine. The "Bromine Present" of Table II is the sum of the bromine added as potassium bromide and that present as impurity in the sodium chloride. When the conditions of titration were such that a stoichiometric ratio was not expected, the appropriate factor obtained from Table I was applied. The calculations for experiment 7 of Table II are given for illustration.

Bromine added: as potassium bromide, 0.8035 mg.; as impurity in 117 mg. of sodium chloride, 0.0012 mg.; total, 0.8047 mg. Approximately 0.75 ml. of 0.04 N chlorine water was used to liberate the bromine, which was absorbed in about 25 mg. of sodium sulfite. Near the end point the potassium bromate was added in 0.04-ml. portions. Fenwick's (*3*) formula indicated the end point at 1.688 ml. of 0.0598 N potassium bromate, corresponding to 0.8068 mg. of bromine. However, an examination of series 6 of Table I shows that the titration under these conditions gives results which average 0.8 per cent too high; subtracting 0.8 per cent or 0.0064 mg., a final corrected value of 0.8004 mg. is obtained.

Table I. Titration of Bromide in the Presence of Moderate Quantities of Chloride

Series	Mole Ratio Cl to Br	Volume at End Point	Acidity	Bromine Present	Bromine Found	Recovery
		Ml.	*N*	*Mg.*	*Mg.*	%
1	0.0	121	6.2	199.3	200.5	100.6
	1.0	121	6.2	199.3	200.7	100.7
	2.0	121	6.2	199.3	200.8	100.7
	3.0	121	6.2	199.3	200.6	100.6
	4.0	121	6.2	199.3	200.5	100.6
2	2.0	166	6.3	199.3	199.7	100.2
	2.0	166	6.3	199.3	199.7	100.2
	2.0	166	6.3	199.3	199.8	100.2
3	0.5	24	6.3	39.94	39.91	99.9
	0.5	24	6.3	39.94	39.99	100.1
	1.0	24	6.3	39.94	39.99	100.1
	1.0	24	6.3	39.94	39.89	99.9
4	0.5	9	6.7	3.991	4.022	100.8
	1.0	9	6.7	3.991	4.009	100.5
	1.0	9	6.7	3.991	4.015	100.7
	2.0	9	6.7	3.991	4.015	100.7
5	1.0	14	5.4	3.991	3.991	100.0
	2.0	14	5.4	3.991	3.991	100.0
	2.0	14	5.4	3.991	3.994	100.1
	2.0	14	5.4	3.991	3.988	99.9
	2.0	14	5.4	3.991	3.996	100.1
6	1.0	4.7	6.4	0.8035	0.8079	100.6
	1.0	4.7	6.4	0.8035	0.8114	101.0
	1.0	4.7	6.4	0.8035	0.8066	100.5
	2.0	4.7	6.4	0.8035	0.8119	101.0
	2.0	4.7	6.4	0.8035	0.8119	101.0
7	1.0	3.3	6.8	0.4006	0.4031	100.6
	2.0	3.3	6.8	0.4006	0.4059	101.3
	2.0	3.3	6.8	0.4006	0.4035	100.7
	2.0	3.3	6.8	0.4006	0.4050	101.1

Table II. Determination of Bromide in Large Excess of Chloride

Expt.	Bromine Present	Bromine Found	Recovery
	Mg.	*Mg.*	%
1	39.94	39.96	100.1
2	39.94	39.88	99.8
3	3.994	3.985	99.8
4	3.994	3.997	100.1
5	3.994	3.995	100.0
6	0.8064	0.8088	100.3
7	0.8047	0.8004	99.5
8	0.8038	0.8018	99.8
9	0.4009	0.3998	99.7
10	0.4009	0.4026	100.4
11	0.4009	0.4017	100.2
12	0.4009	0.4012	100.1

Effects of Iodides

When the iodide content is small relative to the bromide content, no care is necessary to insure its removal. Some experiments were performed in which iodide equivalent to the bromide present was added. By adding at least six equivalents of chlorine water for each equivalent of iodide present, the iodide was completely oxidized to iodic acid and retained in the flask. The subsequent titration showed no evidence of iodide, and gave normal results for the bromide.

Data upon the application of this method to the analysis of urine samples appear in Table III.

Table III. Determination of Bromides in Normal Urine (*2*)

Subject	24-Hour Urine	Bromine Found	Remarks
	Cc.	*Mg.*	
A	1300	13.18	Usual diet Table salt
A	1300	9.32	Usual diet C. P. salt
B	1313	5.50	Usual diet C. P. salt
B	1010	6.60	Usual diet C. P. salt
C	1800	14.70	Usual diet Table salt

Summary

A method for the determination of bromides in the presence of large excess of chlorides has been developed. The bromide is liberated by chlorine water in moderate excess, collected in sodium sulfite solution, and titrated potentiometrically after air oxidation of the excess sulfite. For 4 mg. or more of bromine present as bromide the maximum error is about 0.2 per cent, and for a bromine content of from 0.5 to 1 mg. the error is about 0.5 per cent. Moderate quantities of iodides do not interfere.

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Improved Apparatus for Quantitative Estimation of Helium in Gases

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There are two general methods in use for determining the rare gas content of natural gases. Cady and McFarland (*3*) determined only the helium content, whereas Moureu and Lepape (*13*) estimated the total rare gas content and then further separated it into helium and neon, argon with small amounts of krypton and xenon, and krypton and xenon with small amounts of argon. In both methods use is made of the ability of charcoal, discovered by Dewar (*7*), to adsorb all gases except helium, neon, and hydrogen when cooled in liquid air. It was the experience of Cady and McFarland that hydrogen was freely adsorbed under these conditions, neon much less than hydrogen, and helium very slightly. Their apparatus consisted of a preliminary tube for condensing methane and other hydrocarbons, two tubes filled with charcoal, and two U-dips to condense moisture and mercury vapor, all immersed in liquid air. In addition there were two Plücker tubes, an automatic Sprengel pump, and a tube in which the helium was collected and measured. The purity of the gas was tested by observing its spectrum, and if any nitrogen was found present, the gas was again passed through the charcoal. This is essentially the apparatus which has been used by the U. S. Bureau of Mines and described by Seibel (*16*). Other workers who have used essentially the method of Cady and McFarland are Czako (*6*), McLennan (*12*), Yamada (*18*), Yamaguti and Kano (*19*), Chlopin and Lukasuk (*5*), and Butescu and Atanasiu (*2*). Erdmann (*8*) mixed oxygen with the hydrocarbons and hydrogen and exploded the mixture. Moureu and Lepape burned hydrogen, carbon monoxide, and the hydrocarbons to carbon dioxide and water over heated copper oxide. Carbon dioxide was then absorbed by potassium hydroxide, water by phosphorus pentoxide, and the nitrogen and oxygen were combined with heated calcium or magnesium. When no further pressure drop could be noticed and only the noble gases were distinguishable spectroscopically, the volume of gas was measured. Argon, krypton, and xenon were adsorbed by charcoal cooled with liquid air and the volume of the remaining helium and neon was measured. Through partial vaporization, argon with slight amounts of krypton and xenon is sometimes estimated, or xenon and krypton with slight amounts of argon. Many authors have used at least the principle of the method of Moureu and Lepape. Bamberger (*1*) as well as Ewers (*9*) removed the last traces of nitrogen from the residual gas mixture with oxygen by sparking over potassium hydroxide. Other workers removed the total nitrogen content, after adding oxygen, by sparking over potassium hydroxide and removing the excess oxygen with pyrogallol.

Paneth (*14, 15*) and his students have developed a micromethod by means of which they claim to be able to estimate 10^{-7} cc. of helium with an accuracy of 2 per cent. Sokolov (*17*) has constructed a balance for measuring the density of the unadsorbed helium and neon for use with gases containing at least a helium and neon concentration totaling 0.1 to 0.2 per cent. A method for the continuous separation of helium from a gas mixture by the adsorption of the other gases by charcoal at liquid air temperatures has been described by Cherepennikov (*4*). He also claims to have accomplished the removal of all gases except helium by circulating the gas through charcoal cooled with solid carbon dioxide, regenerating the charcoal after each cycle.

The volume of gas sample used by different workers varies widely. Cady and McFarland used 13 to 15 liters, McLennan about 6 liters, Moureu and Lepape 200 cc., and Paneth, Gehlen, and Peters only 10 cc. With the exception of Chlopin and Lukasuk, who used a modification of an apparatus described by Guye and Germann (*10*), all workers cited have used a complex apparatus. The essential part of the simplification introduced by the latter authors lay in the combination of a vacuum pump, McLeod gage, and storage reservoir. The apparatus described in the present communication is a further adaptation of the apparatus of Guye and Germann to the analysis of helium.

Description of Apparatus

A diagram of the apparatus is given in Figure 1.

The tube *C* containing 30 grams of charcoal serves, when cooled with liquid air, to adsorb all the gases contained in the sample except helium (and some neon). The combination mercury pump and modified McLeod gage *E* serve to create a high vacuum, to measure the volume and pressure of the original sample, to cir-

culate the residual gas over the charcoal, and to collect and measure the residual helium under various reduced pressures. The distance between 1 and the mercury level in D must be less than barometric height. Between 1 and the lower end of E it has a volume of 142.6 cc. The gage and pump also serve as one arm of a manometer to measure the gas pressure. A capillary tube B inserted in the main line and provided with platinum terminals serves as a Plücker tube, but does not have the usual disadvantage of increasing the volume of the apparatus. A and H are filled with fused calcium chloride to keep the air in the manometer tubes clean and dry.

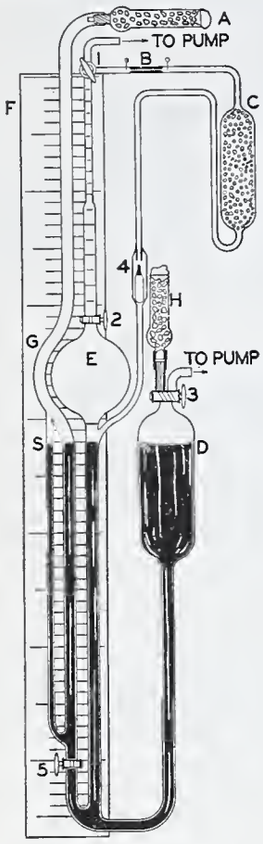

Figure 1. Diagram of Apparatus

By means of the three-way stopcock 1 the apparatus may be evacuated, the gas recirculated over the charcoal, or the system B, C, E evacuated, leaving gas stored in the tube between 1 and 2. By the use of stopcock 2, gas may be pumped from C and connecting tubes and stored in the calibrated tube between cocks 1 and 2 until succeeding strokes of the pump can no longer collect appreciable quantities. Then by leaving cock 1 closed and 2 open the volume and pressure may be determined. The upper part of this tube is calibrated in 0.01 cc. and the lower part in 0.10 cc. The side tube S of the same bore as the upper part of the gage tube may be inserted so as to correct for capillary depression when reading on the upper tube. The right side opening of cock 3 connects to the water pump, serving to make the mercury enter D. The left side is made of a small capillary tube so that if the cock is opened wide to the air, the air enters D slowly and the mercury is prevented from rushing into E too rapidly. At 4 there is a ground joint float which obviates having the mercury rise to a barometric height. It might equally well have been constructed of a porous diaphragm, but evacuation through a porous diaphragm is somewhat slower. Stopcock 5 serves to keep the mercury in G from falling when D is evacuated. An electric heater is conveniently fastened to the metal framework so that it can be placed over the charcoal during preliminary activation. The same support serves to hold the liquid air flask in position. The entire apparatus is mounted on a board surrounded by a molding so as to hold any spilled mercury, and is compact, portable, and easily adaptable to field work.

Experimental Procedure

The apparatus is prepared for an experiment by turning stopcocks 1 and 3 so as to connect with the water aspirator. Stopcock 2 is left open, but 5 is closed. The electric heater is placed over C and is maintained at 360° C. for 1.5 hours. Under these conditions the mercury level is as indicated in the diagram, and the gases liberated in C have a free passage by way of 4, 2, and 1 to the aspirator. By reversing stopcock 3 air is admitted to D and the mercury rises in E. When the mercury reaches stopcock 1, it is closed and compartment D is again evacuated. The valve at 4 closes as the mercury rises, and falls again as soon as the mercury falls in E. The pressure in C is now greater than in E, so that gases pass from C to E. Stopcock 1 is kept closed until, after the next stroke of the pump, the mercury again has almost reached it, when it is opened and the entrapped gas discharged. This is continued after short intervals of time to permit the establishment of pressure equilibrium until no appreciable additional amounts of gas can be removed. The discharge through the Plücker tube B serves as a very convenient indication of the vacuum within. After evacuation with the mercury pump, the discharge is still visible but is usually very weak.

The heater is now removed and the charcoal tube allowed to cool to room temperature. If there is no leak in the apparatus, this cooling brings about sufficient adsorption of the residual gases to prevent any further discharge through the Plücker tube. If the apparatus stands thus overnight without sufficient gas entering to permit a discharge, it may be considered to be free of leaks.

The gas sample is now dried by passing it through concentrated sulfuric acid before it is admitted at stopcock 1. Prior to opening 1, air is allowed to enter at D and the mercury rises to 1. The sample is now admitted through 1, 3 being opened carefully in the direction of the aspirator, and stopcock 5 is opened. A simple calculation will now give the reduced volume of the sample at the particular temperature. Stopcock 5 is now closed and 1 is carefully turned to admit the sample through B to C, which has been previously immersed in liquid air. Stopcock 3 may be opened to the atmosphere, as all the gases except helium and neon are adsorbed in C. The mercury is now allowed to pass stopcock 1. As the gases enter C the liquid air begins to boil vigorously. The residual gases are allowed to remain in contact with the charcoal for 10 minutes to insure complete condensation of all adsorbable gases. If there is any helium present, it is now made evident by the discharge through the Plücker tube. It is convenient to have a tube filled with a sample known to contain helium as a comparison standard mounted close to the apparatus so that both may be viewed with the pocket spectroscope. Some mercury lines will usually be found, but in the authors' case, no neon was visible.

With stopcock 1 still closed, the mercury in E is lowered by evacuating D. As the mercury falls away valve 4 opens, and when the Y passage is cleared the helium residue expands into E. Using the apparatus now as a mercury pump, the gas in E is compressed into the tube between 1 and 2. Stopcock 2 is then closed and the operation repeated. With each stroke of the pump more helium is confined between 1 and 2. After six or eight strokes, there is again no discharge in B. This pumping to a low pressure is necessary to avoid adsorption, since it has been shown by Dewar and later by Homfray (*11*) that 2.5 cc. of helium are adsorbed by 1 gram of charcoal at liquid air temperatures, at atmospheric pressure. Stopcock 5 is opened and the gas volume is measured at various points between 1 and 2 at pressures indicated by the difference in mercury levels in tubes G and E. The actual pressure on the gas is found by subtracting this difference from the barometric pressure. If greater volumes of the gas sample are desired, it is only necessary to pass the helium into C, then pass additional volumes into E.

Experiments were run on gases containing from 0.23 to 0.52 volume per cent of helium. Analyses using all the way from one charge (142.6 cc.) to seven charges (1000 cc., approximately) were made, showing that no increase in accuracy was obtained by using larger samples than 142.6 cc. Results checked each other consistently to 0.01 volume per cent.

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Continuous Determination of Carbonate-Caustic Ratio in a Carbon Dioxide Absorption System

Conductance Apparatus Used in the Bureau of Mines Helium Plant

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An apparatus based on the variation in electrical conductivity accompanying a change in the hydroxide content of a caustic solution, has been installed at the Bureau of Mines Amarillo Helium Plant to give a continuous record of the sodium hydroxide content, or the ratio of sodium carbonate to sodium hydroxide, in a solution used for removing carbon dioxide from natural gas. The instrument indicates the rate at which the hydroxide is reacting with carbon dioxide to form the carbonate, and is adaptable to automatic control of the system for removal of carbon dioxide or to an alarm for indicating a spent solution. It has proved to be sufficiently accurate for plant purposes, to be reliable, and to require but a minimum of attention.

Removal of carbon dioxide from helium-bearing natural gas by scrubbing with a solution of caustic soda is the initial operation at the Amarillo Helium Plant. The spent caustic solution is treated with lime in a recausticizing system and then recycled (*7*). For optimum economy in operation it is essential that when the predetermined ratio of carbonate to caustic at which the solution is considered to be spent is reached, it will be accurately known by a method free from personal error and continuous in performance.

An apparatus, operating on the change in electrical conductivity accompanying the decrease in free hydroxide content of the caustic solution, has been developed for continuous determination of the composition of the solution. Satisfactory results are possible only when the total sodium-ion concentration of the caustic solution remains essentially the same for different batches. The apparatus may be calibrated to read in terms of free caustic, carbonate, or ratio of carbonate to caustic. The rate of conversion of the caustic is also indicated. The apparatus, as described below, has operated satisfactorily for several months and has proved of value.

Theoretical Development

An early application of the method of analysis, which has been used for the apparatus, was made by Cain and Maxwell (*2*) to determine carbon in steel. Later, Hirsch (*3*) proposed to call such a method "conductance analysis." The method has general application, but special consideration must be given each problem.

When two electrolytic solutions are mixed, the conductivity of the resulting mixture cannot, in general, be calculated from the conductivities of the components by the law of simple mixtures, because each component affects the dissociation of the other and changes the total number of ions present. In mixtures containing weak electrolytes it is sufficiently exact, for most purposes, to assume that such electrolytes obey the law of mass action. If the mixture contains only one strong electrolyte its degree of dissociation may be assumed to be practically unchanged by the presence of a weak electrolyte. If there are two or more strong electrolytes present the ionization equilibrium of each component will be influenced by the presence of the ions of the other electrolytes, and calculation of the degree of dissociation is difficult. Arrhenius (*9*) was the first to investigate the relation that must exist between solutions of two electrolytes having a common ion, in order that they may not exert any mutual influence when mixed in any proportions. He demonstrated the isohydric principle showing that when the concentration of the common ion in each of two solutions is the same before mixing no alteration in the degree of ionization occurs after mixing.

Mixtures of hydroxide and carbonate resulting from partial neutralization become isohydric at equivalent ionic concentrations. White (*10*) states a principle, introduced by Arrhenius, which concerns intermediate mixtures: "In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture." White points out that Bray and Hunt (*1*) have tested this principle and have found, in mixtures of sodium chloride and hydrochloric acid, that the measured values of the specific conductance agreed closely with the values calculated on the assumption that the degree of ionization, and therefore the equivalent conductance, of each compound depended on the total concentration.

In the present case, the total alkali concentration, $C_{NaOH} + C_{1/2Na_2CO_3}$, remains unchanged throughout the absorption cycle, except for a maximum dilution of 0.9 per cent per mole of sodium hydroxide converted, and the specific conductance k of any mixture may be calculated, for all practical purposes, from

$$k = \wedge C_{NaOH} + \wedge C_{1/2Na_2CO_3}$$

where

$\wedge$ = equivalent conductance at total alkali concentration
C = concentration in gram equivalents per cc.

The conductance range for use in designing the electrical circuit may be calculated by means of this equation.

The fresh caustic solutions contain approximately 70 grams per liter of sodium hydroxide and 9 grams per liter of sodium carbonate, which is equivalent to a solution containing 76.8 grams per liter of sodium hydroxide, or 1.92 N. The spent solution has an approximate concentration of 9 grams per liter of sodium hydroxide and 90 of sodium carbonate. Since the total alkali concentration remains the same, the equivalent conductance of each compound does not change from its value at 1.92 N. The specific conductance of the two solutions have been calculated by substituting the appropriate values (*4*) in the above equation.

Fresh solution:

$$k_{18^\circ} = 131.8 \times \frac{70}{40.0 \times 1000} + 35.0 \times \frac{9}{53.0 \times 1000}$$
$$= 0.237 \text{ ohm}^{-1}$$

Spent solution:

$$k_{18^\circ} = 131.8 \times \frac{9}{40.0 \times 1000} + 35.0 \times \frac{90}{53.0 \times 1000}$$
$$= 0.089 \text{ ohm}^{-1}$$

The change in specific conductance, corresponding to a change in the specific resistance of

$$\frac{1}{0.089} - \frac{1}{0.237} = 7.0 \text{ ohms}$$

is ample for accurate measurements with an instrument suitable for plant installation.

This method of analysis postulates a constant sodium-ion content. Owing to dilution from the reaction, the normality of the caustic solution with respect to sodium ions decreases as the conversion to carbonate proceeds. The error resulting from dilution may be practically eliminated by an empirical calibration since the effect remains essentially the same for different batches. It is desirable to evaluate the error introduced both by a change in sodium-ion content during the reaction and also by different initial concentrations to determine the applicability of an apparatus for continuous analysis.

The normality of the caustic solution with respect to sodium is changed from 1.92 to 1.89, through a theoretical dilution of 0.9 per cent per mole of sodium hydroxide converted. This corresponds to a change in specific resistance of from 7.0 to 6.9 ohms, which is equivalent to a 2.16 per cent change in the weight per cent ratio of sodium carbonate to sodium hydroxide. A change of normality of 1 per cent during conversion, therefore, causes an error of 1.3 per cent in the ratio. The effect of different initial concentrations may be calculated in the same manner by determining the change in ratio corresponding to an assumed change in concentration. It is calculated that a change in normality of 1 per cent from the value on which the calibration of an apparatus is based will cause an error of 0.9 per cent in the measured ratio.

General Design of Apparatus

Electrical methods in analytical work are becoming more commonly used because of their rapidity, accuracy, and adaptation to control. The design of the apparatus follows the standard practice for industrial application, as exemplified in numerous commercial instruments using the Wheatstone-bridge method for measurement of resistance—for example, in instruments for measuring condenser leakage and boiler-water concentration.

Measurements of conductivity are subject to a positive error due to polarization of the electrodes. This error may be minimized and made practically negligible by a combined use of properly prepared electrodes, large electrode area, a high-frequency current, and a high-resistance cell. Jones and Josephs (*5*) recommend the use of cells having high cell constants (length divided by cross section) so that the resistance to be measured will be large, thereby reducing polarization and heating effects in the cells. Convenient installation at the Amarillo Helium Plant requires the use of 60-cycle current, and the high conductivity of the solution makes it necessary to reduce the electrode area and increase the spacing to increase the cell constant. Constructional difficulties limit the size of the cell, so that while the cell constant is as large as practicable the resistance is yet small. The electrodes are platinized to reduce the polarization error.

By using a balanced Wheatstone bridge a detecting instrument of high sensitivity may be employed with the small current required. Readings are also practically independent of variation in line voltage, and the accuracy of measurement is not influenced by changes in the characteristics of the indicating instrument, since the latter indicates only the null point.

The caustic solution contains impurities such as calcium, silicon, magnesium, iron, and aluminum compounds in small amounts, but probably in sufficient quantity to affect the agreement between the calculated and the measured resistance of the solution. To exclude as many variables as possible it would be desirable, if practicable, to eliminate the effect of impurities by making relative measurements using two cells, one containing the fresh solution and the other containing the solution as it is cycled. It is not possible to do this in the installation described because measurements of the relative change in resistance would require the same ratio of sodium hydroxide to sodium carbonate in each batch of fresh solution to be cycled. It is impracticable to obtain this in plant operation. A fixed resistor having a resistance equivalent to the average of that of the fresh solutions is used in place of a second cell. The error introduced by using only one cell is small and decreases as the solution becomes spent. Although the initial content of sodium hydroxide may differ in the various batches, the total alkali content is approximately the same in each case, and the ratio of carbonate to caustic at which the solution is considered to be spent is fixed at a definite value. To protect the electrodes in the cell and prevent a change in surface area, a solution filter is placed before the cell.

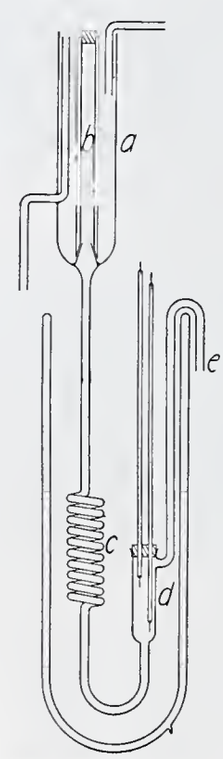

Figure 1. Diagram of Apparatus

The circulating caustic solution is at temperatures ranging from 65° to 35° C. Temperature compensation cannot be accomplished by the usual method of manual or automatic adjustment of a resistance in the bridge circuit because of the variable composition of the solution. For that reason the conductivity cell is thermostated. The solution, however, must be precooled before final adjustment of the temperature in the thermostat.

It has been proved experimentally (*5*) that under some conditions the use of water in the thermostat and the grounding of the thermostat may result in serious errors due to three causes: (1) Capacitance is introduced by the grounded conducting liquid in the thermostat, (2) the walls of the glass cell may act as a dielectric in a condenser, allowing alternating

current to flow outside the cell and thus decrease the measured resistance of the cell, and (3) the alternating current in the cell may induce eddy currents in the water outside the cell, having the effect of increasing the apparent resistance. The errors from these causes are directly proportional to the cell resistance and to the frequency and may amount to 0.5 per cent in extreme cases.

Under conditions where errors resulting from use of water would be serious, oil may be used as the thermostat liquid. However, in the installation at the Amarillo Helium Plant the error introduced into the measurements by the use of water as the thermostat liquid is considered to be less than 0.1 per cent because of the relatively low resistance of the cell and the comparatively low frequency of the current. Consequently, advantage has been taken of some of the more desirable physical properties of water as a thermostat liquid in using it rather than oil without introducing an appreciable error.

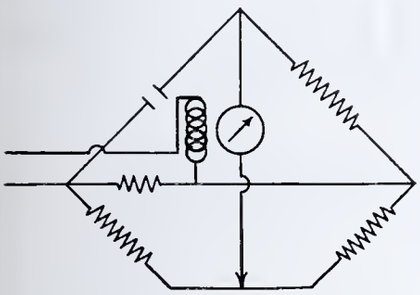

Figure 2. Electrical Circuit

Construction of Apparatus

Figure 1 indicates the arrangement of the conductivity apparatus as finally constructed.

A regulated flow of solution through the cell is obtained with the constant-head device *a*. The solution is filtered through the alundum tube *b*, and its temperature is equalized in the coil *c*, which is immersed in the thermostat with the cell *d*. The solution is discharged into the drain at *e*. The conductivity cell contains the two electrodes, which are platinum wires fused into soda-glass tubes. The electrode spacing is adjustable. Electrical connection is made through mercury which fills the tubes. The thermostat is a large Dewar tube filled with water, the temperature of which is controlled at 30° C. by a toluene-mercury thermoregulator operating an immersion heater. The water is stirred by a slow stream of air.

The electrical circuit is shown in Figure 2. Since no resistance-recording instrument was available, a Leeds & Northrup potentiometer recorder was adapted for use as a conductance-measuring instrument. This was done by replacing the galvanometer assembly with one designed for alternating current and by replacing the potentiometer circuit with a Wheatstone-bridge arrangement. The 110-volt source of alternating current was supplied to the galvanometer field coil and the bridge through a 1 to 1 insulating transformer because it was difficult to prevent current leakage from the immersion heater. To insure the currents through the galvanometer and through the bridge circuit being in phase the potential of 4 volts for the bridge was taken from the galvanometer-field coil circuit by means of a potential divider. (This arrangement of the recorder and electrical circuit follows standard practice in commercial conductivity recorders.)

Calibration of Apparatus

Four solutions were made up from the spent and the fresh caustic for preliminary calibration, their compositions being determined by the method of Winkler (*8*). Data for calibration were also calculated for the solutions, but the agreement was not close, probably because the effect of the impurities in the solution had not been taken into account and because of inaccuracies in obtaining a cell constant (apparatus for precise conductivity measurements was not available). The preliminary results served only to establish the trend of the calibration curve. Since the apparatus was designed for use under plant conditions it was essential that its calibration should agree well with routine analytical results. Final calibration was made while the instrument was in operation. Recorder readings were taken, at the times the periodic analyses of the solution were made, over a period of several weeks. The data obtained are plotted in Figure 3. The curves are drawn only for the range of the instrument, although their courses have been determined by calculation and extrapolation to zero sodium hydroxide and sodium carbonate contents.

Operation and Reliability of Apparatus

As installed in the Amarillo Helium Plant, the apparatus has required attention only in cleaning the filter daily and the electrodes occasionally. The alundum filter used must be porous enough to filter rapidly and yet must retain the extremely fine suspended material in the caustic solution which seems to collect first upon the electrodes. Alundum tubes made of mixture RA-68 (Norton Co.) have proved satisfactory for the filter. With the filter cleaned daily, the surfaces of the electrodes remain apparently unchanged for several weeks. As frequently as experience shows it to be necessary the electrodes should be cleaned, rinsed in distilled water, and plated with platinum black deposited from a 10 per cent platinic chloride solution containing 0.025 per cent of lead acetate. Current for the plating may be supplied from one or two dry cells, reversing the polarity of the electrodes every 30 seconds.

The lag in the apparatus is largely determined by the rate of overflow at the filter. In the installation described this may be as rapid as desired, since the overflow is returned to the system. The rate of flow through the cell should be slow enough to insure equalization of the temperature, and may be adjusted by changing the liquid head or by using a capillary in the line after the filter. The normal rate of flow through the cell is about 10 cc. per minute.

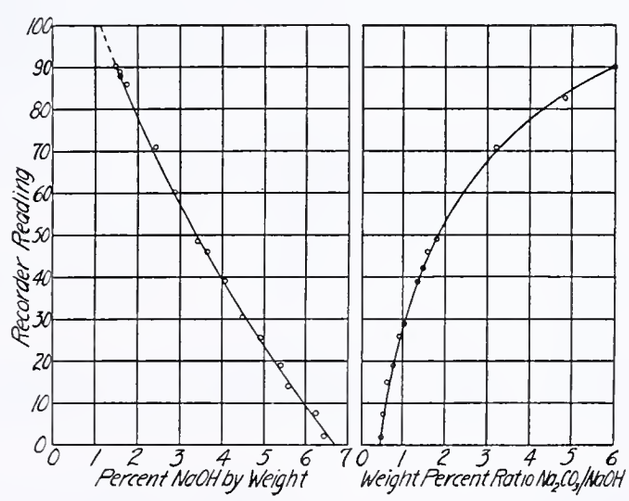

Figure 3. Calibration Curves

In estimating the accuracy of the apparatus, variations in frequency, impurities, dilution, and total alkali content must be considered, as well as the sensitivity of the recorder. With a frequency of about 1000 cycles, the error due to polarization, which is always present when current passes through an electrolyte and which causes a discrepancy between the true and apparent resistance, is small with platinized electrodes if the resistance is above a critical value. It has been empirically determined (*6*) that the error introduced by reducing the frequency below 1000 cycles varies, approximately, inversely as the square root of the frequency within the range 60 to 1000 cycles. If the error in measurement is 0.1 per cent at 1000 cycles, about 0.4 per cent error will be introduced at 60 cycles. If the cell is calibrated at 60 cycles this error may be considered negligible.

In the installation described calibration is made at 60 cycles, and discrepancies caused by variation in line frequency need not be considered in the relative measurements. The most serious source of error is expected to be that due to variations in total alkali content. Based on results obtained with the apparatus in use under plant conditions, the precision of the instrument may be given as ±2 per cent of the ratio of carbonate to caustic.

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Determination of Inorganic Salts in Sulfonated Oils

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In the committee discussion prior to the adoption of Commercial Standard CS43-32 of the Bureau of Standards for the grading of sulfonated (sulfated) oils, a simple method was abandoned because of the lack of an adequate method for determining alkali sulfates and chlorides in such products. A new method is here outlined that determines these salts readily and accurately. It depends upon the fact that dehydrated sulfonated oils become miscible with carbon tetrachloride in the presence of oleic acid and the inorganic salts are insoluble in the mixed solvent. The addition of oleic acid directly to the oil also prevents the sample from jellying upon being dehydrated. Moreover, by this method the salts are determined in the combination in which they actually exist in the original oil.

New titration methods for sodium carbonate and acetate are also described, since these salts react with oleic acid and cannot be determined by the previous method. The titration methods are based on the following findings:

Total fatty matter in a sulfonated oil may be extracted quantitatively and without decomposition with ether over an acidified solution of salt.

Acetic acid dissolved in ether may be extracted practically completely by proper washing with salt solution.

Sodium acetate may be quantitatively decomposed, liberating acetic acid, by heating with excess oleic acid at 123° to 125° C.

Sulfonated oil containing soap may be heated for 30 minutes at 123° to 125° C. with practically no decomposition of the organically combined sulfate group.

Incidental to manufacture or through admixture, commercial sulfonated oils may contain various amounts of inorganic salts, such as alkali chlorides, sulfates, and less frequently acetates, carbonates, etc. The determination of inorganic sulfate in sulfonated oils is part of the regular procedure for finding organically combined sulfuric anhydride by the barium sulfate methods, but the other inorganic salts are practically always included with the "undetermined," largely because no satisfactory direct method of analysis for inorganic salts has been described. A satisfactory method would not only round out the analysis of a sulfonated oil but would also be of great assistance in grading or classifying such products. Thus, in connection with Commercial Standard CS43-32 of the Bureau of Standards (*3*), the committee was in favor of grading sulfonated oils by subtracting from 100 per cent the sum of the moisture and inorganic salts, but this method had to be abandoned because the methods for determining inorganic salts were unsatisfactory.

Herbig (*8*) determines inorganic sulfate by dissolving the sample in ether, washing with a saturated solution of sodium chloride, and precipitating the sulfate in the wash water with barium chloride. To overcome troublesome emulsions, which highly sulfonated oils tend to form, he replaces one third of the ether with benzene. If emulsions still persist, Herbig dissolves the oil in absolute alcohol, filters, dissolves the residue in hot water and determines the inorganic sulfate in the filtrate. Nishizawa (*10*) attributes these emulsions to the comparatively easy solubility of the normal or disodium salt of sulfonated oils in concentrated sodium chloride solution, and further states that the compound is salted out with considerable difficulty even in the presence of solid sodium chloride. On the other hand, the monosodium salt is practically insoluble in saturated sodium chloride solution. Accordingly he modifies the Herbig method by first converting the compound to the monosodium salt with hydrochloric acid, using methyl orange as the indicator.

In the official method of the Wissenschaftliche Zentralstelle für Öl- und Fettforschung (*12*) a mixture of 40 per cent ether and 60 per cent amyl alcohol is used as solvent for the oil; otherwise the procedure is the same as the Herbig benzene-ether method (*8*). Burton and Robertshaw (*2*) determine total inorganic salts by digesting the dehydrated sample with alcohol or alcohol-ether, filtering, dissolving the residue in hot water, and determining the solids in the filtrate by evaporation. The inorganic salts, they state, are not completely precipitated with alcohol in the case of many sulfated oils. Some tests made in this laboratory indicate that the Burton and Robertshaw method may yield good results with sodium sulfate but is not satisfactory with sodium chloride using 95 per cent alcohol as one of the solvents. The results on a sample, in which the inorganic salts contained about 90 per cent sodium chloride and the rest sodium sulfate, were as follows:

Solvent	Inorganic Salts Added	Inorganic Salts Found
	%	%
2 parts ethyl ether and 1 part 95 per cent alcohol	7.84	6.32
2 parts ethyl ether and 1 part absolute alcohol	7.84	7.52

Difficulties may also be experienced with the alcohol-ether solvent in the case of dehydrated oils containing at the same time large amounts of fatty glycerides or mineral oils, and neutral soap. The former are sparsely soluble in alcohol and the latter in ether.

Another method for total inorganic salts is that of Hart (*4, 5*). According to this method, total nonvolatile inorganic salts are determined indirectly from the ash, fixed alkalinity, and organically combined sulfuric anhydride in the sample. This procedure is also the official method of the American Leather Chemists Association (*1*). It yields reliable and accurate results, except in the presence of ammonium salts and sodium acetate; the former is volatilized during the ignition and the latter changed to the carbonate. Moreover the formulas are calculated for sodium salts and in the presence of potassium it becomes necessary to determine the metallic elements.

McBain and McClutchie (*9*) state that soda soaps dissolve and form jellies in nonpolar solvents, such as benzene, xylene, etc.,

and also that sodium oleate and stearate exhibit no signs of gelation in acetone or chloroform.

The writer finds that sulfonated oils, particularly when neutralized and dehydrated, dissolve in ethyl ether or carbon tetrachloride with great difficulty, giving practically nonfilterable solutions. However, the dehydrated oil becomes miscible with these solvents upon the addition of oleic acid. Taking advantage of this fact and also of the practically negligible solubility of sodium chloride and sulfate in ether or carbon tetrachloride, a method for determining these salts in sulfonated oils has been developed. It consists essentially of dehydrating the sample in the presence of oleic acid, dissolving in ether or carbon tetrachloride, and filtering off the residue. The use of oleic acid as a coupling agent and for liquefying soap-solvent gels is well known (*7*). Oleic acid or its equivalent is invariably used in the determination of water in soap by the distillation method (*6*) to prevent foaming and to keep the solvents liquid. Carbon tetrachloride, suggested by R. A. Pingree, was found to be the best of several solvents tested. This method was developed as a part of an investigation being carried out by a subcommittee on sulfonated oils, appointed by the American Association of Textile Chemists and Colorists.

Procedure for Alkali Sulfates and Chlorides

Weigh 3 to 5 grams of the sample into a 250-cc. beaker, add an approximately equal amount of oleic acid and about 0.5 cc. of 1 *N* caustic soda, and heat in an oil bath to 105–110° C. until practically water-free. Then raise the temperature to 118–120° C., keeping it there for about 5 minutes. The dehydrated sample should remain liquid and homogeneous upon cooling, otherwise more oleic acid is required. Dissolve the dehydrated sample in 100 cc. of carbon tetrachloride (50° to 55° C.) and filter through a Gooch crucible or through a counterpoised filter paper. The last traces of the residue may readily be transferred by allowing the solvent to evaporate, when the salt is easily detached from the glass wall. Wash the residue with three 15-cc. portions of a 2 per cent solution of oleic acid in carbon tetrachloride, warmed to 50–55° C., and then with six 15-cc. portions of hot carbon tetrachloride and two 15-cc. portions of ether, or until free from oil, care being taken that the top of the filter is thoroughly washed. Dry at 125° to 130° C. for 45 minutes, and repeat drying until constant weight is obtained. The residue is finally ignited and again heated to constant weight. The last weight is taken as the final result. Any appreciable difference between the "dried" and "ignited" residues indicates either volatile salts or fatty matter. Obviously in the presence of ammonium or other volatile salts, the "dried" residue should be taken as the final result.

The ordinary sulfonated oil was found to be stable when heated as outlined as long as there was some soap present, even as little as 2.0 per cent on the weight of the sample. There was also no reaction between the salt and the free fatty acids upon heating. This was shown by the fact that the alkalinities of a sample containing salt were identical before and after heating. If a reaction did occur, soap would form and the alkalinity of the sample would be correspondingly increased. Evidently alkali added to stabilize the oil will not affect the result, provided it is all converted into soap. Oleic acid is added to the carbon tetrachloride in the first washings in order to prevent precipitation of soap on the residue. The determination of the dried as well as the ignited residue is suggested in order to detect the presence of insoluble fatty matter or ammonium salts, or incomplete washing. The residue, of course, may be analyzed for its constituents by the usual methods for inorganic analysis. It is to be noted that this method yields the alkali salts in the form actually present in the original oil, including chlorides which are not determined by the barium sulfate method.

In Table I are listed sulfonated products, containing sodium or ammonium sulfate or sodium chloride, that were analyzed for their salt content by the solvent method and, in a few cases, also by the Herbig or barium sulfate method. The figures represent the averages of several analyses. The differences in the amount of sodium sulfate by the two methods for samples 1 and 2, given in the last column, were 0.04 and 0.08 per cent, respectively, and for sample 3 containing ammonium sulfate the difference was 0.21 per cent. Sample 4 showed 4.93 per cent of sodium chloride by the solvent method, compared with 4.91 per cent added. In all cases the residues upon ignition, with the exception of sample 8, showed a slight loss. Sample 8 is a special product, brought on the market within the past few years as a detergent, and is supposedly a condensation product of a fatty acid and a sulfonated amino compound. Ignition of the dried residues was accompanied by slight charring, apparently due to adsorbed fatty matter. In the remaining samples listed in Table I, the reliability of the solvent method is indicated by the small differences in weight between the "dried" and "ignited" residues. That soaps of saturated fatty acids do not interfere with the method is shown by sample 6, representing a neutralized sulfonated tallow, which upon ignition lost only 0.12 per cent.

Table I. Inorganic Sulfates and Chlorides in Sulfonated Oils

Sample	Description	Nature of Salt	Inorganic Salt: Solvent method: Dried	Solvent method: Ignited	Solvent method: Difference	Barium sulfate method	Difference
			%	%	%	%	%
1	Sulfonated castor oil	Na_2SO_4	0.92	0.83	0.09	0.79	0.04
2	Sulfonated castor oil	Na_2SO_4	6.72	6.64	0.08	6.56	0.08
3	Sulfonated castor oil	$(NH_4)_2SO_4$	8.52	..	..	8.73	0.21
4	Sulfonated castor oil	NaCl Na_2SO_4	5.00	4.93[b]	0.07	..	..
5	Highly sulfonated oil[a]	Na_2SO_4	2.92	2.84	0.08	..	..
6	Sulfonated tallow	Na_2SO_4	6.41	6.29	0.12	..	..
7	Sulfonated mineral oil	Na_2SO_4	0.25	0.22	0.03	..	..
8	Sulfonated detergent[c]	NaCl Na_2SO_4	18.52	17.75	0.77	..	..

[a] 93 per cent sulfonated.
[b] Added 4.91 per cent.
[c] Commercial sample of a condensation product of a fatty acid and a sulfonated amino compound.

Table II. Sodium Sulfate in Sulfonated Castor Oils

Analyst	Sodium Sulfate: Sample C: Solvent method	Sample C: Barium sulfate method	Sample C-1: Solvent method	Sample C-1: Barium sulfate method
	%	%	%	%
1	0.74	0.75	6.74	6.22
2	0.83	0.79	6.64	6.56
3	0.78	0.76	6.68	6.55
4	0.81	0.76	6.64	6.03
5	0.81	0.85	6.55	6.90
6	0.95	0.71	6.86	7.16
Grand av.	0.82	0.77	6.68	6.57
Greatest difference	0.21	0.14	0.31	1.13
Av. deviation from mean	0.05	0.03	0.08	0.31

To determine the possibility of agreement among different analysts using the solvent method, members of the American Association of Textile Chemists and Colorists subcommittee on sulfonated oils were asked to analyze by the new method two samples of sulfonated castor oil, samples C and C-1, containing various amounts of sodium sulfate. For purpose of comparison, the samples were also analyzed by the barium sulfate method. The results, which represent the averages of check analyses, are given in Table II. It will be observed that for sample C the average was 0.82 per cent by the solvent method and 0.77 per cent by the gravimetric method, or a difference of only 0.05 per cent; and for sample C-1 the results were 6.68 and 6.57 per cent, respectively, or a difference of 0.11 per cent. The agreement in results for sample C-1, as shown by the greatest difference and the average deviation from the mean, was considerably better for the solvent method than the gravimetric method—namely, 0.31 and 0.08 per cent compared with 1.13 and 0.31 per cent, respectively.

Determination of Sodium Acetate and Sodium Carbonate

The solvent method unfortunately cannot be used in the presence of sodium acetate or carbonate, since these salts react with the free fatty acids to form soap when the oil is dehydrated. It has also been found that solid sodium acetate, thrown out of the neutralized oil during dehydration, reacts quantitatively with the excess oleic acid added to the solvent to effect solution of the oil. This reaction takes place even at temperatures below the boiling point of the solvent. Trotman (*11*) made experiments to determine whether different proportions of oleic acid are able to decompose sodium acetate completely when distilled with steam. When only small quantities were used, decomposition was practically complete, the acetic acid in the distillate corresponding to the whole of oleic acid taken. When larger quantities of oleic acid were taken, only a portion was recovered as acetic acid.

A method available for acetate is to determine the acetic acid by steam distillation with phosphoric acid. However, the volatility of fatty acids (*11*) with steam and the presence of carbonate may interfere with the accuracy of this method. Alkali carbonates may be determined as in soap analysis, by taking advantage of their insolubility in alcohol. The dehydrated sample is digested in absolute alcohol or with a mixture of ether, and the residue after filtration is washed free of titratable salts, such as sodium acetate, etc. The residue is then dissolved in hot water and the carbonate determined in the filtrate by titration.

More rapid and convenient titration methods for both alkali carbonates and acetates have been developed in this laboratory and seem to be accurate within 0.2 per cent. Since sodium acetate cannot be accurately titrated with the usual indicators because of free acetic acid, it becomes necessary to remove the acid either by volatilization or by washing. The titration methods are based on the following findings: Total fatty matter in a sulfonated oil may be extracted quantitatively without decomposition with ether over an acidified solution of salt; acetic acid dissolved in ether may be extracted practically completely by proper washing with salt solution; sodium acetate may be quantitatively decomposed, liberating acetic acid, by heating with excess oleic acid at 123° to 125° C.; and a sulfonated oil containing soap may be heated for 30 minutes at 123° to 125° C. with practically no decomposition of the organically combined sulfate group. The titration method is varied somewhat, depending upon whether or not the sample contains carbonates, acetates, or both.

Procedure in Presence of Carbonates Only

Alkalinity as Soap (A_s). Dissolve 5 grams of the sample in 100 cc. of water contained in a separatory funnel and add 25 grams of sodium chloride, 5 drops of 0.1 per cent solution of methyl orange, and 60 cc. of ether. Titrate with 0.5 N sulfuric acid until distinctly acid (about 2 cc. excess), shake well, and allow the layers to separate. Wash the ether layer with two 25-cc. portions of saturated salt solution and the combined water layers with 30 cc. of ether. Retain the water layers for the following determination. Combine the ether layers, add 0.5 cc. of 0.5 N caustic soda, evaporate the bulk of the ether, add 100 cc. of neutral alcohol, and titrate with 0.5 N sodium hydroxide until neutral to phenolphthalein. The result (as well as all other alkalinities) is expressed in milligrams of potassium hydroxide per gram of sample and represents the alkalinity corresponding to the soap (A_s).

Total Alkalinity (A_t). This test is similar to the determination of total alkali in soaps. The combined water layers from the previous analysis are boiled to expel carbon dioxide and the titration is completed. The result equals the sum of the alkalinities corresponding to the soap (A_s) and carbonate (A_c), or

$$A_t = A_s + A_c$$

Hence,

$$\% \text{ sodium carbonate} = \frac{(1)}{(10)} \frac{Na_2CO_3}{2\ KOH} (A_t - A_s) = 0.09447\ (A_t - A_s)$$

Procedure in Presence of Acetates Only

Alkalinity as Free Fatty Acids (A_f). Follow the usual procedure for free fatty acids—namely, dissolve 5 to 10 grams of the sample in 100 cc. of neutral alcohol, warm if necessary, and titrate with 0.5 N sodium hydroxide until neutral to phenolphthalein. Calculate the result as milligrams of potassium hydroxide per gram of sample.

Combined Alkalinity as Soap (A_s) and as Free Fatty Acids (A_f). Dissolve 5 grams of the sample in 100 cc. of water contained in a separatory funnel and add 25 grams of sodium chloride, 5 drops of 0.1 per cent methyl orange solution, and 60 cc. of ether. Add an excess of approximately 0.5 N sulfuric acid (about 2 cc. excess), shake well and allow to separate. Wash the ether layer with three 100-cc. portions of concentrated salt solution or until neutral to phenolphthalein. Discard the water layers. The ether layer is then treated and titrated as under "alkalinity as soap" above. The result in this case represents the combined alkalinities of the soap (A_s) and of the free fatty acids (A_f). The alkalinity of the soap is evidently the difference between this determination and the alkalinity of the free fatty acids.

Total Alkalinity (A_t). Heat with constant stirring 5 grams of the sample with approximately twice its weight of oleic acid in a 250-cc. beaker, immersed in an oil bath, for 30 minutes at 123° to 125° C. Dissolve in 50 cc. of water, add 5 drops of methyl orange solution, and titrate with 0.5 N sulfuric acid until distinctly acid (about 2 cc. excess). Transfer to a separatory funnel, add sodium chloride to make a 25 per cent solution, and extract with four 75-cc. portions of ether or until the ether layer is practically neutral to phenolphthalein. Discard the ether layers, rinse the funnel with water, and complete the titration in the combined water layers. The titration represents the combined alkalinities of the soap and the acetate (A_h), or

$$A_t = A_s + A_h$$

Hence, sodium acetate may be calculated from the following formula:

$$\% \text{ sodium acetate} = \frac{(1)}{(10)} \frac{NaAc}{KOH} (A_t - A_s) = 0.1462\ (A_t - A_s)$$

Procedure in Presence of Sodium Carbonate and Sodium Acetate

Alkalinity as Soap (A_s). The fat is extracted, washed, and titrated as in "combined alkalinity as soap and as free fatty acids" above. The wash waters, however, are retained for the following test. Evidently in the presence of carbonates there can be no free fatty acids present; hence, the result represents the alkalinity corresponding to total soap (A_s).

Alkalinity as Soap (A_s) and as Carbonate (A_c). The combined water layers from the previous determination are heated under an air condenser to expel carbon dioxide. The condenser is then washed down with water and the titration of the contents completed until neutral to phenolphthalein. The titration obviously represents the combined alkalinities of the soap and carbonate. Hence, the difference between the last two determinations represents the alkalinity of the carbonate (A_c), from which the per cent of sodium carbonate may be calculated as follows:

$$\% \text{ sodium carbonate} = \frac{(1)}{(10)} \frac{Na_2CO_3}{2\ KOH} A_c = 0.09447\ A_c$$

Total Alkalinity (A_t). This is determined exactly as in the presence of acetates only. The result represents the combined alkalinities of soap, carbonate, and acetate, or

$$A_t = (A_s + A_c) + A_h$$

The alkalinity of the acetate may now be determined since all the other terms are known. The per cent of sodium acetate may then be calculated from the corresponding alkalinity by the following formula:

$$\% \text{ sodium acetate} = \frac{(1)}{(10)} \frac{NaAc}{KOH} (A_h) = 0.1462\ (A_h)$$

Three samples of oil, containing known amounts of sodium carbonate, sodium acetate, and a mixture of the two, were analyzed according to the titration methods and the results

Table III. Alkali Carbonates and Acetates in Sulfonated Oils by New Titration Methods

	Sample A	Sample B	Sample C
	Mg. KOH/*g.*	*Mg.* KOH/*g.*	*Mg.* KOH/*g.*
Alkalinity as free fatty acids (A_f)			
Found	0.00	4.5	0.00
Calculated	0.00	4.4	0.00
Alkalinity as soap (A_s)			
Found	34.0	28.4	34.2
Calculated	33.4	29.0	33.4
Total alkalinity (A_t)			
Found	59.2	49.9	56.9
Calculated	59.8	49.6	56.9
Alkalinity as soap (A_s) and as carbonate (A_c)			
Found	...	...	45.9
Calculated	...	...	46.6
Sodium carbonate	%	%	%
Found	2.38	..	1.11
Calculated	2.49	..	1.25
Difference	0.11	..	0.14
Sodium acetate			
Found	..	3.14	1.61
Calculated	..	3.01	1.51
Difference	..	0.13	0.10

are given in Table III. Sample A was made by mixing a titrated solution of sodium carbonate with an equal amount of a neutralized sulfonated oil of known alkalinity. Sample B was a mixture of a titrated solution of acetic acid exactly neutralized with caustic soda, and an equal amount of a sulfonated oil with known alkalinity and acidity. Sample C was a mixture of 25 per cent each of the carbonate and acetate solutions, and 50 per cent of the neutralized sulfonated oil. The results in Table III are the averages of several determinations in each case. It will be noted that the amount of sodium carbonate found in sample A differed from the calculated value by 0.11 per cent, that the difference in sodium acetate for sample B was 0.13 per cent, and the differences in sodium carbonate and sodium acetate for sample C were 0.14 and 0.10 per cent, respectively. The accuracy of these results is well within the experimental error and is considered satisfactory for the analysis of sulfonated oils.

Acknowledgment

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Determination of Alpha-Cellulose

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The test for alpha-cellulose has long been a matter of controversy. In 1911 Jentgen (*1*) suggested a test for resistant cellulose and advised its use in determining the suitability of fibers for viscose manufacture. Since that time so many other suggestions have been made, most of them mere variations of Jentgen's original test, that tests have been drawn up by a committee of the Division of Cellulose Chemistry of the American Chemical Society (*3*) and by the German Chemical Society (*4*). In both cases, however, the methods are purely empirical, the determination having been chosen which gives the most consistent results. This is admitted to be true and everyone recognizes the limitations in using the determination.

The concentration of the alkali used in the treatment of cellulose by these two methods is of importance. In the present research a sample of paper was treated with sodium hydroxide of strength varying from 1 to 17.5 per cent for 45 minutes and for 24 hours at room temperature following the procedure prescribed by the American Chemical Society's committee. The data are offered in Table I and are plotted in Figure 1.

Table I. Effect of Time and Concentration of Alkali

Sodium Hydroxide	Alpha-Cellulose 45 minutes	Alpha-Cellulose 24 hours
%	%	%
1	96.27	95.78
2	93.22	91.94
4	91.48	90.73
10	88.74	87.41
17.5	87.94	86.40

It will be seen that the effect of the concentration of the alkali is much greater than the effect of time, after some period less than 45 minutes. For this reason, runs were made with 17.5 per cent sodium hydroxide on a sample of pulp for 2, 5, 10, 30, and 45 minutes, and on a sample of absorbent cotton for 1, 2, 5, 10, and 50 minutes. The method proposed by the divisional committee of the American Chemical Society was followed as far as possible. The period after maceration was changed as required for runs down to 15 minutes' total mercerization. Runs of 10 minutes' duration were treated with the alkali in four parts, 2.5 minutes apart, and were macerated continuously. Runs of 5 minutes or less were treated with the total volume of alkali all at once and were macerated for the full time. The results of durations less than one minute were variable and showed that the solution failed to wet the sample completely or to have sufficient contact to act uniformly on the sample. The data are given in Table II and are plotted in Figure 2.

Table II. Effect of Time

(17.5 per cent sodium hydroxide used)

Time	Alpha-Cellulose Cotton	Alpha-Cellulose Pulp
Min.	%	%
1	98.9	..
2	98.8	88.2
5	98.7	87.5
10	98.7	86.5
30	..	86.4
45	..	86.1
50	98.5	..

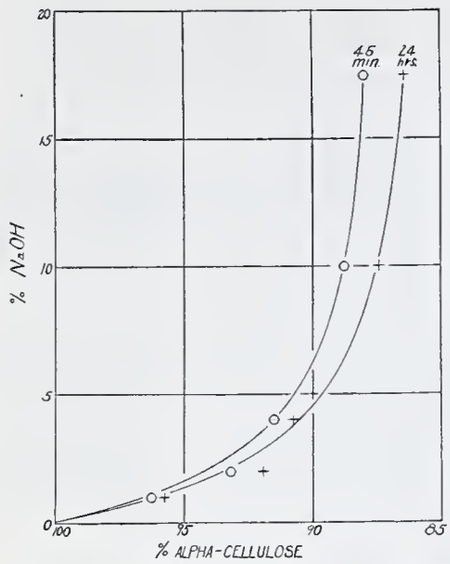

FIGURE 1. EFFECT OF TIME AND CONCENTRATION OF ALKALI

In both cases, there is a great loss suffered by the cellulose in the first few minutes of reaction, and this rate of loss suddenly decreases until the cellulose becomes nearly nonreactive. Apparently the time before this break occurs and the sharpness of the break depend upon the source of the cellulose used.

If the alpha-cellulose is attacked much more slowly than the non-alpha-cellulosic part of the material, we can easily explain the forms of these curves. The non-alpha-cellulosic part is peptized more rapidly until it is almost gone, the loss of alpha-cellulose during this interval being very small. This is represented by the horizontal portion of the curves. When this part is nearly all peptized, the rate of loss immediately falls off because the attack on the alpha-cellulose is very slow. The nearly vertical rise in the curves brings this out clearly. The position and form of the break in the curve will, of course, depend on the sample used. If it is almost pure alpha-cellulose, as in the case of cotton, the amount of impurities will be small and will be removed quickly. The break in the curve will be sharp. If there is much material in addition to the alpha-cellulose in the sample, it will take longer to remove it, and the change from the period when the main reaction is the taking out of impurities, to the period when there is only a slow attack on the alpha-cellulose, will be more gradual.

A second series of runs was made using 10 instead of 17.5 per cent sodium hydroxide. The pulp was the same as that used with the stronger alkali, in the preceding experiment. The results of this treatment are given in Table III and plotted in Figure 2.

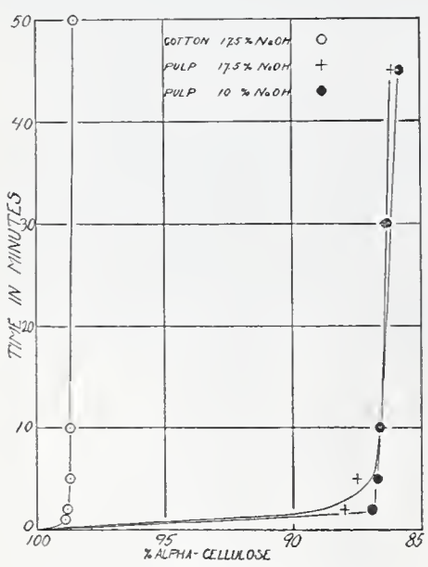

FIGURE 2. EFFECT OF TIME AND CONCENTRATION ON ALPHA-CELLULOSE FROM COTTON AND PULP

Although the 10 per cent alkali is more effective in the shorter times, both 10 and 17.5 per cent solutions give the same values after 45 minutes of reaction. From this one sample it would appear that the 10 per cent alkali changes the shape of the curve at the break somewhat.

From the data of Neale (*2*) we can calculate roughly the end concentration of the sodium hydroxide solutions. He gives the following figures obtained by the change in titer method: initial concentration, 5.17 equivalents per liter; adsorption, 0.486 to 0.493 equivalents per mole of cellulose. By taking the adsorption of the cotton in the 17.5 per cent sodium hydroxide (5.25 equivalents per liter) to be 0.490, one is able to determine approximately the reduction of the concentration in the solutions during the treatment. With a 3-gram sample using 75 cc. of 17.5 per cent sodium hydroxide, the concentration will fall only 0.4 per cent, so that the end concentration will be 17.1 per cent. A 4-gram sample will reduce the concentration to 17.0 per cent and a 2-gram sample to 17.2 per cent. The size of the sample therefore need not always be exactly 3 grams.

At least one author (*5*) offers the suggestion that the losses in alpha-cellulose suffered during the aging of alkali pulps in the viscose process are due to oxidation by the air. However, the action must be very slow. Identical samples of absorbent cotton were treated with 17.5 per cent sodium hydroxide at room temperature for 50 hours. Both were in stoppered flasks. Through one, air was bubbled which had passed through 17.5 per cent sodium hydroxide previously. The residues recovered were: air-free, 98.7 per cent; air-saturated, 98.6 per cent. The effect of oxygen in the air, then, for any alkali treatment using cold 17.5 per cent sodium hydroxide can be neglected.

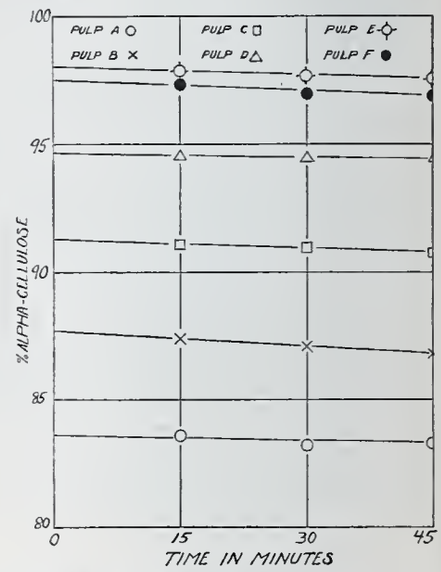

FIGURE 3. DETERMINATION OF ALPHA-CELLULOSE IN COMMERCIAL PULPS

TABLE III. EFFECT OF TIME

(10 per cent sodium hydroxide used)

TIME	ALPHA-CELLULOSE
Min.	%
2	86.88
	86.90
5	86.78
	86.56
10	86.54
	86.65
30	86.34
	86.32
45	86.04
	85.72

PROPOSED METHOD

In view of these facts, the author proposes for the present a method for the determination of alpha-cellulose which is based on the stability of the cellulose to attack by sodium hydroxide. Samples are run according to the method proposed by the AMERICAN CHEMICAL SOCIETY'S committee for two or three different times, say, 15, 30, and 45 minutes. These times should be sufficient to cause the points to fall on the vertical flat of a curve similar to those in Figure 2. By extrapolation back to zero time, the alpha-cellulose content of the original sample should be given.

It is claimed as an advantage of this method over any other, that the time factor is eliminated. No standard time is necessary; in fact, as long as the points lie well beyond the break, the times may be chosen to suit the sample or convenience. Since the attack on the alpha-cellulose is slow,

extreme accuracy in measuring the time of reaction is not necessary. Slight error in time will result in practically no error in the ultimate alpha-cellulose result. The ratio of the sample to the reagent need not be exact, provided it is within certain limits (1 to 4 grams in 75 cc. of solution). The main precaution seems to be the use of carbonate-free alkali throughout the treatment.

The suggested method has been tested on six commercial paper pulps, the alpha-cellulose content of which had been determined previously by the manufacturer, and the results are shown in Table IV and in Figure 3.

Table IV. Determination of Alpha-Cellulose in Commercial Pulps

Pulp	Manufacturer's Value	Per Cent Residue after: 15 min.	30 min.	45 min.	Value by: Calculation	Curve
A	84.02	83.03	82.95	83.57	83.60	83.75
		83.75	83.36	82.97		
		84.02	83.14	83.50		
B	87.63	87.44	87.08	86.88	87.69	87.50
		87.35	87.07			
C	91.26	91.01	91.10	90.75	91.21	91.25
		91.15	90.76	90.80		
		91.06	90.67	90.74		
D	94.90	94.54	94.44	94.46	94.56	94.60
E	98.54	97.87	97.70	97.63	97.89	97.97
F	98.42	97.33	96.97	96.94	97.28	97.10

It was found more convenient and perhaps a little more accurate to calculate the percentage of alpha-cellulose back to zero time than to plot the data and estimate the value from the extrapolated curve. This was done by determining the loss for the 15-minute periods, 15 to 30 minutes' reaction and 30 to 45 minutes' reaction. The average of these two is designated $\Delta\%/\Delta T$. Using the 15-, 30-, and 45-minute values as bases, the alpha-cellulose at zero time can be calculated by adding to these values $\Delta\%/\Delta T$, $2\Delta\%/\Delta T$, and $3\Delta\%/\Delta T$, respectively. For example, using the data from pulp F:

Difference in Loss from: 15 to 30 min.	30 to 45 min.	%/T	Alpha-Cellulose Calculated from: 15 %	30 %	45 %	Average %
17	7	12	97.99	97.94	97.99	97.97

The average of these zero values is taken as the calculated result. The method of calculating gets rid of any errors in plotting and drawing the curve and in estimating the extrapolated value.

Summary

A preliminary study of the effect of concentration of alkali on the tentative standard method proposed by the Division of Cellulose Chemistry of the American Chemical Society determination of alpha-cellulose was made.

In studying the effect of time on the treatment of cellulose with 17.5 per cent sodium hydroxide a characteristic curve was found which showed rapid losses in weight of cellulose at first and soon approached a nearly constant value. A curve of the same type giving the same nearly constant value was found for 10 per cent sodium hydroxide.

A method for the determination of alpha-cellulose has been proposed temporarily which eliminates exact specifications of time and sample-reagent ratio. The suggested method has been tested on six commercial pulps.

Acknowledgment

The six pulp samples used in testing the method suggested above were furnished, together with the manufacturer's data, through the kindness of G. A. Richter of the Brown Company. Other pulp stock was furnished by the Strathmore Paper Company.

The author is indebted to Professor Bancroft for suggestions and criticism in this work.

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Determination of Sulfur in Benzene or Gasoline

Modification of A. S. T. M. Lamp

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In a recent article, Gillis (*2*) describes a modification of the standard A. S. T. M. lamp which provides for better control of the flame. A similar lamp of somewhat simpler construction has been in use in the author's laboratory for about three years, and has been particularly successful with benzene and its blends, which ordinarily give more trouble than gasoline itself.

The modified lamp is sketched in Figure 1. The glass tube *A*, which carries the wick as in the standard A. S. T. M. lamp, is made somewhat longer than usual to accommodate the sleeve *B*, which is a glass tube of slightly larger diameter. Because of the variation in tubing diameters, it has been found advisable to make the sleeve of tubing sufficiently larger than *A* to require some sort of flexible packing which provides the necessary friction to hold the sleeve in place. If a glass-to-glass friction be used, sticking is likely to occur at a most inopportune moment, with disastrous results. Even a smooth-sliding sleeve as made up may bind in use, because of expansion of the inner tube when heated by the combustion of the material under test. A small piece of cotton wicking in the annular space serves as a satisfactory packing material.

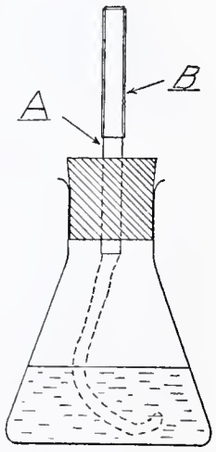

Figure 1

In operation the sleeve is simply moved up and down on the tube carrying the wick. If the flame is too high, the sleeve is pushed up, and vice versa. Very close adjustment may be made by rotating the sleeve slightly as it is moved up or down.

The principle of flame control in this lamp is apparently the same as that employed in one of the lamps proposed by Edgar and Calingaert (*1*) who used a movable brass outer tube, but its construction is simpler, and the control, in the author's experience, more satisfactory.

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Received December 9, 1933.

Improved Analyzer for Carbon Monoxide in Air

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A CONTINUOUS carbon monoxide recorder for small concentrations in air has been described by Fieldner, Katz, and Meiter (*1*), and by Katz and others (*3*). In this apparatus the oxidation of the carbon monoxide as it comes in contact with a granular catalyst results in a temperature rise in the air stream within the catalyst cell, which is transmitted to a recording potentiometer through a series of differential thermocouples. The cell potential is directly proportional to the carbon monoxide concentration in the absence of readily oxidizable or inhibiting impurities which affect the catalyst.

To remove moisture and other condensable constituents the air sample is passed through a train of concentrated sulfuric acid, soda-lime and charcoal, and calcium chloride, previous to passing through the hopcalite catalyst. Fourteen instruments of this type were installed at the Holland Tunnel (*2*) where they record carbon monoxide in the seven exhaust air ducts leading from each of the two tubes for vehicular traffic between New Jersey and Manhattan. In practice the use of sulfuric acid as an air drier is objectionable because of its corrosive nature and the difficulties of frequent renewal and disposal. This led to the development of a modified form of the analyzer, which is here described. The acid train whose chief function is the removal of moisture has been replaced by duplicate adsorbers using either silica gel or activated alumina. Alumina of 1.2 to 2.4 mm. size was used in tests on this apparatus and in the preliminary tests reported in this paper.

Description of Apparatus

Continuous drying is obtained by alternating the adsorbers and activating the adsorbent between periods of use by means of a heater inside each cylinder. Interchange of cylinders is effected by synchronized four-way cocks which determine the direction of air flow in each cylinder. The other parts of the original Katz analyzer have been rearranged and modified for suction flow supplied by a rotary blower, whereby the air sample enters the apparatus directly instead of first passing through the blower and then to the apparatus. This arrangement eliminates the possibility of contamination of the adsorbent or the catalyst by oil spray from the blower.

The adsorbers *A* and *B* in Figures 1 and 2 have an inner adsorbent cylinder of 8.9-cm. (3.5-inch) brass tubing, 40 cm. long, filled with 1.2-mm. to 2.4-mm. (8- to 14-mesh) alumina to within 10 cm. of the top. This tube is surrounded by a 2.5-cm. jacket through which cooling water flows during the cooling period following activation of the adsorbent and throughout the succeeding 8-hour period in which the adsorbent is drying air. This is surrounded by a 2.5-cm. jacket of loose asbestos to improve the conservation and distribution of heat in the adsorbent during the activation, when the jacket is empty and contributing to the insulation of the adsorbent. The unit *a*, Figure 2, for supplying the activating heat to the passing air stream is a 200-watt element from a reflector heater suspended from a cover plate through which two spark plugs, *b*, are screwed for terminal connections. The heater circuits are connected to limit switches, *W*, shown in Figure 1, which control the sequence of heating through contact with fingers on the cooling water cocks, *c* and *d*.

The analyzer is connected to the 110-volt alternating current electrical supply through the 2-pole fused switch, *t*, Figure 1, to which the three-heat immersion heater inside boiler *C* is connected directly. The supply to the motor and activating heaters passes through an overload relay magnetic switch, *u*, which cuts off the supply to the heaters when the motor stops. A push button, *v*, starts and stops the motor and heaters independent of the boiler supply.

Below the adsorbers are water tube air coolers, *e*, Figure 2, surrounded by water in the cooling reservoir *D*, which cool the moisture-laden air from each adsorber when it is being activated by the downward passage of hot air. The coolers communicate with catch bulbs below and with the four-way cock, *f*. This cock turns simultaneously through a vertical connecting bar with the upper four-way cock, *g*, communicating with the top of the adsorbers.

The three-way cock, *h*, is connected to the inlet side of cock *g* and is the means of providing additional air while activating to insure a more even heat distribution in the adsorbent. Following activation this air, since it contains moisture, is not allowed to enter the cooling adsorbent but is diverted through by-pass *i* to the blower, *r*, by a turn of the cock. The quantity of air passing into this three-way cock is regulated by plug cocks *j* to give a temperature not greater than 340° C. at the top of the alumina and not less than 150° C. at the bottom.

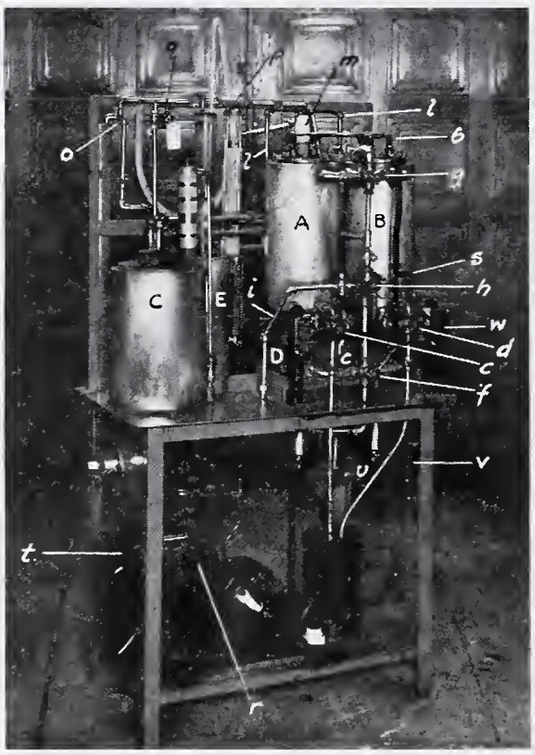

Figure 1. Continuous Analyzer for Carbon Monoxide in Air

Cooling water enters at both ends of reservoir *D* through valves *k*, and passes through the tubes of the coolers to the center. Three-way cocks *c* and *d* admit water from the reservoir to the cooling jackets of the adsorbers or empty them as required.

Precautions were taken to insure a proper operating sequence by the use of the blocking cross bars, *s*, Figure 1, attached to the vertical connecting bar, which synchronize the movement of water cocks *c* and *d* with the position of the four-way air cocks.

The water when flowing through the jackets passes through the outlet tubes, *l*, whose ends are water-sealed in adjoining overflow compartments in trap *m*, from which the water passes to the steam bath condenser of the cell assembly, *C*. The water trap compartments are joined by a small hole which allows water to pass from either side to seal both tubes against entrance of air when one adsorber jacket has been emptied. A jacket is drained previous to activating the adsorbent through the three-way cocks *c* or *d* by which process air enters to displace the water through the overflow compartment in the water trap, *m*.

A cylinder of 330 cc. of charcoal, *n*, removes quantities of hydrocarbon vapors from the air sample which

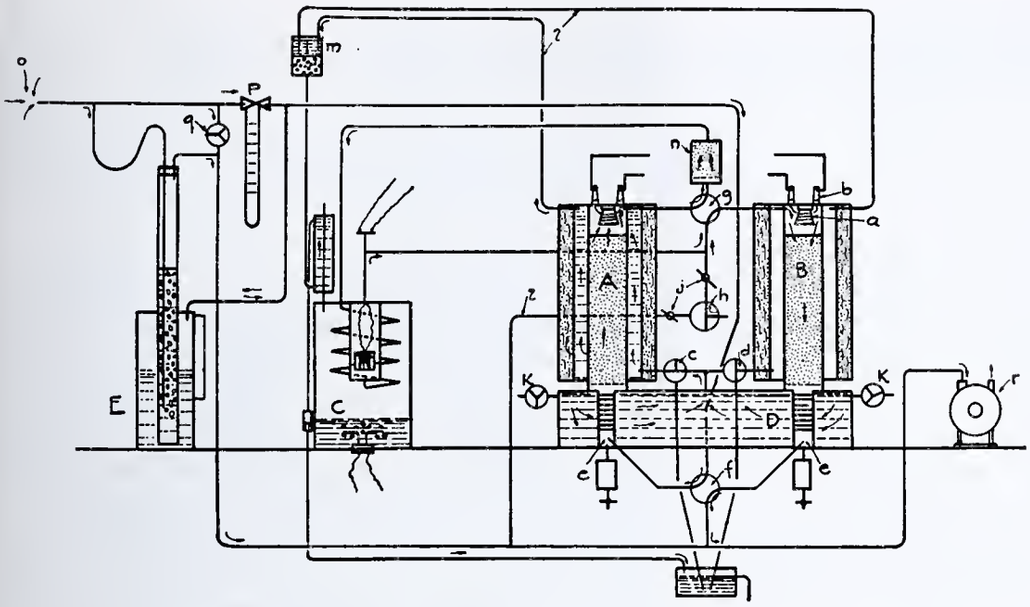

FIGURE 2. FLOW DIAGRAM OF CARBON MONOXIDE ANALYZER

might affect the accuracy of the analyzing cell. This has a screw cap at one end for periodical replacement of the activated charcoal.

OPERATION

The air sample is continuously drawn into the apparatus at *o*. That in excess of 12 liters per minute to the flowmeter, *p*, by-passes through the regulating valve, *q*, and through the flow compensator, *E*, directly to the blower, *r*.

At the point of sequence illustrated in Figure 2, the regulated flow from the flowmeter passes into cock *f* and upward through adsorber *A*, through charcoal cylinder *n*, and into the preheating coil inside the steam bath at *C*, from which it passes through the catalyst chamber also enclosed by the steam bath. The return air from the catalyst chamber reënters the four-way cock, *g*, together with additional air from the room for activating purposes through three-way cock *h*. The increased flow of about 30 liters per minute enters adsorber *B* and passes downward over the heater and through the adsorbent which at the end of 4 to 6 hours acquires a temperature of about 320° C. at the top and 180° C. at the bottom. The air leaves the adsorber through the after-cooler, *e*, from which it reënters the four-way cock, *f*, and joins the previously by-passed air to the blower, *r*.

At the end of the 4- to 6-hour activating period the water cock, *d*, is turned 90° to fill the water jacket of the activated adsorber, and the auxiliary air entering cock *h* is diverted to the blower by a 90° turn of the cock. A finger on the water cock has contacted a limit switch which shuts off the activating heater. Adsorber *A* continues to dry the air sample and adsorber *B* receives the dry return air from the cell until the end of the 8-hour period.

At the end of the 8-hour period the four-way cocks, the water cock below adsorber *A*, and the three-way air cock, *h*, are turned 90°, whereby the path of the air sample is transferred from *A* to *B*, water is drained from the cooling jacket of *A*, the limit switch is actuated to start the heater, and room air is diverted into *A* for activation of the adsorbent. The operations mentioned before are repeated in succeeding cycles, commencing with the turning of cocks *c* and *h* at the end of 4 to 6 hours to cool the activated adsorbent in *A*.

A drying period of 8 hours per adsorber was selected because it allows a convenient time for reactivating and cooling and because it coincides with the working hours of operators who would operate the analyzer when in service. The rate of flow of 12 liters per minute produced the best sensitivity in the catalyst cell with a minimum of variation for small changes in air velocity.

AIR-DRYING TESTS

Preliminary tests at a flow rate of 15 liters per minute, using adsorbers roughly similar in form to these described, were used as a basis for determining the cylinder size required for the 8-hour period.

These adsorbers were constructed of 22-gage sheet iron, were 51 cm. long, and contained an inner adsorbent cylinder 10.2 cm. in diameter which was surrounded by a concentric 2.5-cm. air jacket. One of the cylinders was further jacketed with a 2.5-cm. layer of asbestos over the air jacket. The 8- to 14-mesh alumina, obtained in 1931, was reactivated downward with heaters suspended above the adsorbent as in the analyzer described. Thermocouples placed in the top and bottom of the adsorbent beds indicated temperatures of activation and adsorption.

In tests made with these adsorbers and with the analyzer later constructed, air saturated by bubbling through a bottle of water at room temperature and precooling at 12.8° to 21.7° C. was passed through the activated alumina and the effluent air was tested at intervals for moisture with a weighed tube of phosphorus pentoxide. The air dryness determinations for these tests appear in Figure 3, which shows the relation between grams of moisture per cubic meter of air and the time from start of the run when the dryness tests were made.

Other data in connection with the tests are given in Table I. The quantity of moisture adsorbed is calculated from the moisture entering in the saturated air at the temperature stated, corrected for moisture which passed through the adsorbent.

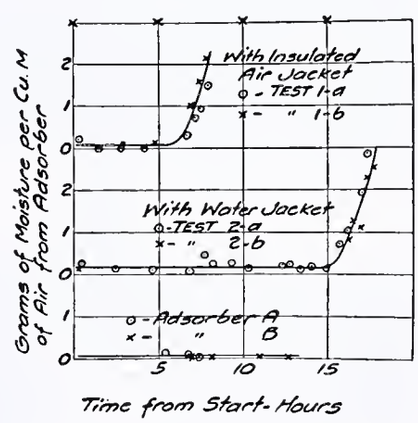

FIGURE 3. EFFECT OF WATER JACKET AROUND CYLINDER OF ACTIVATED ALUMINA ADSORBENT

The object of tests 1 and 2 was to determine the effective drying period of the activated alumina adsorbent with and without water-cooling. In test 1, 2.2 kg. of the alumina were activated and tested for adsorption in check runs 1a and 1b in the asbestos-insulated air-jacketed cylinder. In test 2 an equal quantity of alumina was similarly tested in a cylinder of the same size with water passing through the jacket during adsorption. The relative efficiencies of the adsorbent under these two conditions are indicated in Figure 3.

A laboratory test on adsorbers *A* and *B* of the assembled analyzer is reported in test 3 of Table I. The apparatus was run as for the continuous analysis of air, with one ad-

sorber being activated as the other dried the air. It was shut down overnight and the activated alumina was allowed to cool with water flowing through the jacket. These tests were not continued to the break point in efficiency of the adsorbent.

TABLE I. ADSORPTION TESTS WITH ACTIVATED ALUMINA USING SATURATED AIR

	Test 1a[a]	Test 1b[a]	Test 2a[b]	Test 2b[b]	Test 3[c] Adsorber A	Test 3[c] Adsorber B
Activation temperatures, ° C.						
Near top of alumina	279	310	260	254	316	332
Near bottom of alumina	254	266	232	229	149	204
Adsorption temperatures, ° C.[d]						
Near top of alumina	66	67	38			
Near bottom of alumina		60	39		32	35
Entering air						
Saturation temperatures, ° C.	18.1	19.4	21.1	21.7	12.8	12.8
Flow, liters per min.	15	15	15	15 to 16	12	12
Moisture, grams per cu. meter	15.6	16.5	18.2	19.0	11.2	11.2
Period of complete drying, hours	6.0	6.0	15.0	15.0	8.1[e]	13.5[e]
Flow of air, cu. meters	5.4	5.4	13.5	13.5	5.8	9.7
Estimated moisture adsorbed						
Grams	84	89	245	255	65	108
Per cent of activated alumina	3.8	4.0	11.1	11.6	4.6	7.8
Cooling water						
Approximate flow, liters per hour			90	90	90	135
Temperature, ° C.			21.1	21.7	12.8	12.8

[a] 22-gage sheet-iron adsorber; adsorbent cylinder, 10.2 × 51 cm., 0.08-cm. wall; air jacket and asbestos covering; 2.2 kg. of alumina.
[b] 22-gage sheet-iron adsorber; adsorbent cylinder, 10.2 × 51 cm., 0.08-cm. wall; water jacket; 2.2 kg. of alumina.
[c] 16-gage, 3.5-inch brass tube; adsorbent cylinder, 8.9 × 40 cm., 0.13-cm. wall; water jacket; 1.4 kg. of alumina.
[d] As indicated when adsorption zone reached level of thermocouple junctions.
[e] Test discontinued before break in adsorbent efficiency.

Following these tests the experimental analyzer was connected to an air-sampling line in parallel with the analyzer regularly in service on this line and continuous carbon monoxide records were obtained from both analyzers for several months ending in June, 1932. The air sampled came from an upgrade section of the south tube of the Holland Tunnel. The agreement of the parallel records was satisfactory and the hopcalite cell sensitivity remained normal throughout the period.

Discussion

The curve of test 1 in Figure 3 indicates a break point in adsorption in the insulated adsorber at 6 hours from the start of the test, at which point moisture in the effluent increased rapidly. Before this break in drying efficiency the effluent contained less than 0.14 gram of moisture per kilogram of air (1 grain per pound) or less than 0.18 gram per cubic meter. Test 2 curve indicates a similar break point at 15 hours for the same quantity of alumina in the same size cylinder when water-cooled. Part of the moisture found in the effluent in test 2a apparently came from moisture adsorbed at the top of the bed before the test began and again at 7.5 hours from the start of the test when the run was stopped overnight. The adsorptive capacity of the alumina was multiplied three times by the 21° to 29° C. of cooling effected by the water. The dry alumina had adsorbed 3.9 per cent of its weight of moisture in test 1 and 11.4 per cent in test 2 when moisture broke through.

No gain of moisture in the effluent air from adsorbers *A* and *B* was found for the periods of test. The average moisture content of the air coming from adsorber *A* was 0.07 gram per cubic meter of air and from adsorber *B*, 0.04 gram.

The effective adsorptive capacities remaining in adsorbers *A* and *B* when the runs were stopped are estimated at 60 and 30 per cent, respectively, based on the 11.4 per cent capacity of activated alumina shown in test 2. The probable effective drying period of the 1.4 kg. of alumina in each of these adsorbers with saturated air flowing at 12 liters per minute and at a temperature of 21.1° C. (70° F.) is 11.9 hours. This estimate is based on the results obtained in test 2 with 2.2 kg. of alumina and a rate of flow of 15 liters per minute.

Since the cooling water temperature limits the quantity of moisture which the air sample may carry through the precooler, the maximum quantity of adsorbent required for a definite period of air-drying with cooling water may then be fairly accurately known. It is desirable in a carbon monoxide recorder to reduce to a minimum the time of passage of air from the point of sampling to the analyzing cell, and some advantage is therefore gained by having the internal volume of the adsorber as small as the volume of adsorbent will permit. The added efficiency gained by the use of cooling water as shown in tests 1 and 2 permits considerable reduction in the size of the adsorber. In this case the quantity of alumina actually required for 60 liters of saturated air (1 liter per minute for 1 hour) with cooling water at 21.1° C. (70° F.) was 10 grams or 12 cc.

Summary

The carbon monoxide recorder is an important control instrument in the ventilation of the Holland Vehicular Tunnel. Special maintenance and some hazard are involved in the use of sulfuric acid in the air-drying and purifying train of the original design. For this reason a substitute drier was developed which consists of duplicate cylinders containing granular adsorbent. This is reactivated in place as the analyzer continues to operate by a heater inside the cylinder, assisted in part by the recirculation of the dry return air from the analyzing unit of the recorder.

Since preliminary tests indicated the desirability of cooling the adsorbent during use to increase drying capacity, the adsorbers are jacketed for cooling with water. The water is drained from the jacket during the activating period, but the activating air stream passes through a cooler as it leaves the adsorbent.

The maintenance required for the operation of the analyzer consists of valve manipulation twice in every 8 hours or other drying period selected, and removal of water from the condensation trap below the adsorbers as required. Although the possibility of simplification of valve arrangement and other parts of the apparatus has become apparent its operation was satisfactorily carried on by the operators in charge of ventilating equipment in the building.

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(2) Katz and Frevert, Ind. Eng. Chem., 20, 564 (1928).
(3) Katz et al., U. S. Bur. Mines, *Tech. Paper* 355.

Received December 23, 1933.

Correction. Our attention has been called to a minor inaccuracy in our article "Extraction of Triethanolamine Oleate from Aqueous Solution," appearing in Ind. Eng. Chem., Anal. Ed., 6, 78 (1934). The statement was made, referring to extraction of fatty acid from triethanolamine soaps, "Normally, soaps other than those of abietic acid are not decomposed by extraction of an aqueous solution with ethyl ether." We should have added "by recognized methods," since small amounts of fatty acid are extracted from aqueous solutions of neutral soap by ethyl ether. This is adequately provided for in the usual methods.

This in no way invalidates our conclusions, since the extraction of oleic acid was high in experiments 2 and 5, in which 0.05 *M* triethanolamine, the alkali of the soap under discussion, was present in excess. Frank M. Biffen and Foster Dee Snell

Mixed Perchloric and Sulfuric Acids

I. Simultaneous Oxidizing and Reducing Properties of Hot Concentrated Perchloric Acid

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THE oxidation reactions of hot, concentrated perchloric acid are the basis of important reactions of quantitative analysis (*3*, *6*). The intensity of these oxidations is greatly influenced by the extent to which the acid has been dehydrated. With hot acid of strength greater than that corresponding to the formula $O_2H_5ClO_4$ (*4*), simultaneous reducing properties are in evidence. These reducing properties are accounted for if either hydrogen peroxide or ozone is present in traces as a result of the decomposition. Reactions corresponding with this explanation can easily be demonstrated. The acid strength of 70 to 72 per cent perchloric acid is conveniently increased to 85 per cent or higher by the addition of sufficient 96 per cent sulfuric acid or fuming sulfuric acid. For many reactions of analytical importance, these principles require a close study of conditions. It is the purpose of this paper to describe the general aspects of this subject.

Decomposition in Presence and Absence of Mild Reducing Agents

By concentrated perchloric acid, this paper refers to that strength between 70 and 85 per cent $HClO_4$ by weight (roughly, that concentration between dioxonium perchlorate and oxonium perchlorate, $O_2H_5ClO_4$ and OH_3ClO_4). Hot, concentrated perchloric acid decomposes mainly according to reaction 1. A secondary reaction, 2, is also possible to a slight extent.

$$4HClO_4 \longrightarrow 2Cl_2 + 7O_2 + 2H_2O \quad (1)$$
$$2HClO_4 \longrightarrow Cl_2 + 3O_2 + H_2O_2 \quad (2)$$

Both reactions are intensified in proportion as the concentration increases. Reaction 3 indicates the formation of oxonium perchlorate using concentrated or fuming sulfuric acid.

$$O_2H_5ClO_4 + H_2SO_4 \longrightarrow OH_3ClO_4 + H_2SO_4 \text{ (hydrated)} \quad (3)$$

An important example of a reaction using hot concentrated perchloric acid as an oxidizing agent is the oxidation of trivalent chromium to the hexavalent state in the process of Willard and Gibson (*6*) for the quantitative estimation of chromium in chromite, ferrochrome, and stainless steel. In a study of this method, Lundell, Hoffman, and Bright (*2*) state that the oxidation is never quite complete. The following reaction is shown to be quantitative only to the extent of 99.5 per cent completion:

$$Cr_2O_3 + 2HClO_4 \longrightarrow 2CrO_3 + H_2O + Cl_2 + 2O_2 \quad (4)$$

If chlorine and oxygen are the only decomposition products, it is difficult to offer a reason for this. In the presence of a small amount of hydrogen peroxide the following reaction explains the fact:

$$2CrO_3 + 6HClO_4 + 3H_2O_2 \longrightarrow 2Cr(ClO_4)_3 + 3O_2 + 6H_2O \quad (5)$$

Reactions 1 and 4 are much more intense than 2 and 5. The difference accounts for the 0.5 per cent reversal of reaction 4. Reactions 2 and 4 are intensified by increasing the strength of perchloric acid. By properly regulating conditions of time, temperature, and acidity, the Willard and Gibson method (*6*) can be made to give more accurate results, as will be shown in a subsequent paper. The influence of hydrogen peroxide as described may easily be duplicated by the addition of a trace of it to a hot, dilute solution of chromic acid in perchloric acid. The chromium is instantly reduced to green chromic ion.

Oxidation of Chromic Oxide to Chromic Acid

Two hundred milligrams of chromic oxide were treated with 50 ml. of oxonium perchlorate (84.79 per cent $HClO_4$) and heated to 168° C. The reaction mixture was allowed to cool. Red crystals of chromic oxide, insoluble in concentrated perchloric acid, formed and the acid was colorless. Upon standing 12 hours at room temperature, the acid became colored owing to the presence of green chromic perchlorate. Repeating the heating of the acid and oxidation of chromium, the results are duplicated (reactions 4 and 5).

The oxidation of chromic oxide was tested with increasing strengths of perchloric acid produced from various proportions of 15 per cent fuming sulfuric acid and 72 per cent perchloric acid (Table I). Parallel experiments were made replacing chromic oxide by small amounts of manganese perchlorate, $Mn(ClO_4)_2 \cdot 6H_2O$. The manganese was momentarily oxidized to permanganate and the reaction rapidly reversed as shown by the immediate decolorization due to hydrogen peroxide formed simultaneously. The reaction is intensified in the presence of a little phosphoric acid.

Table I. Oxidation of Chromium and Manganese by Concentrated Perchloric and Sulfuric Acids

Sulfuric Acid 15 per cent fuming	Perchloric Acid 72 per cent	Temperature after Mixing From 25° C. to	Cr_2O_3 Oxidation to Cr_2O_3	Mn^{++} Oxidation to MnO_4^-
Ml.	*Ml.*	° *C.*	° *C.*	° *C.*
10	10	82.0	136	150
12	8	84.4	128	137
13.3	6.6	86.5	120	128
15	5	88.4	119	125
10 (95 %)	10	40.0	168	...

The heat attained upon mixing the acids of Table I is an indication of the extent to which the perchloric acid has been dehydrated. By using 75 per cent sulfuric acid, a mixture with 72 per cent perchloric acid results in no appreciable evolution of heat. The temperature after mixing was observed in a 30-ml. Dewar test tube, evacuated but not silvered, and the temperature maximum found using a small Anschütz thermometer.

It will be seen that the dehydration of perchloric acid by the sulfuric acid in all cases was equivalent, at least, to the formation of oxonium perchlorate, since the temperature at which the chromium was oxidized is equal to or less than that required by the 84.79 per cent perchloric acid as previously described. The greater the dehydration of perchloric acid, the lower is the temperature of oxidation. In all cases in Table I the oxidation of chromium was clearly reversed to an obvious extent, as shown by the color change resulting upon allowing the solutions to cool and stand. In the case of the higher concentrations of perchloric acid, the reduction was complete in a few hours. This indicates the magnitude of hydrogen peroxide formation as governed by perchloric acid concentration.

Oxidation of Trivalent Cerium to Tetravalent State

Solutions of cerous perchlorate in hot, concentrated perchloric acid are not oxidized to ceric perchlorate at 168° to 200° C. Mixtures of equal parts of 96 per cent sulfuric acid and 72 per cent perchloric acid oxidize cerous sulfate readily to ceric sulfate at approximately 140° C. The reaction is as follows:

$$7Ce_2(SO_4)_3 + 2HClO_4 + 7H_2SO_4 \longrightarrow 14\,Ce(SO_4)_2 + Cl_2 + 8H_2O \quad (6)$$

Ceric sulfate is insoluble in 75 to 95 per cent sulfuric acid and in the reaction mixture of acids outlined above. The substitution of 75 for 96 per cent sulfuric acid is found to result in more complete oxidation of cerium at 185° C. In accordance with the principles previously described, this is accounted for through the practical elimination of hydrogen peroxide as a minor decomposition product of hot, concentrated perchloric acid.

The principle of reaction 6 has been applied to the preparation of ceric sulfate, both in the form of the anhydrous salt and in its addition compounds with ammonium sulfate. The data are included in a subsequent paper. Ceric perchlorate has been prepared in solution by the electrolytic oxidation of cerous perchlorate in a perchloric acid solution by Fichter and Jenny (*1*). It is possible that a mixture of perchloric and sulfuric acids may be found desirable in the quantitative determination of cerium. A preliminary study has been made with favorable results.

Uses for Mixed Acids in Analytical Studies

The many advantages found in the determination of chromium following perchloric acid oxidation (*6*) make the method popular in routine plant control analyses. With technical grades of 68 to 70 per cent perchloric acid (free from chromium) the method is less costly. By employing mixtures of perchloric and sulfuric acids, the method can be cheapened further and at the same time other advantages besides economy in the cost of perchloric acid can be shown.

Mixed perchloric and sulfuric acids have been used satisfactorily in the oxidation of potassium ferro- and ferricyanides to liberate the ferric ion as a standard procedure in the evaluation of titanous solutions. Perchloric acid alone can be used in this case, but the method is cheaper using the mixed acids.

The addition of perchloric acid to 96 per cent sulfuric acid for the destruction of organic matter in the familiar Kjeldahl nitrogen determination has been proposed. Attempts to diminish the time of digestion following this process have proved highly successful. Unfortunately, the process in certain applications gives low results, presumably due to loss of nitrogen in the digestion period. If the concentration of sulfuric acid is lowered to 75 per cent and the 72 per cent perchloric acid is then added to the hot sulfuric acid, the oxidizing power is not materially diminished and there is little tendency toward the formation of hydrogen peroxide as a decomposition product. The change thus proposed may eliminate the disturbing reactions previously mentioned. The problem is being investigated in these laboratories.

The dehydration of silica by hot, concentrated perchloric acid in the method of Willard and Cake (*5*) has become an important analytical procedure. With a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid, the intensity of the dehydration may be sufficiently high without showing a tendency to convert the perchlorates present to sulfates. Such an application would result in the obvious advantage of economy in cost of perchloric acid where it is applicable. The subject is being investigated.

If the dehydration of perchloric acid by sulfuric acid is objectionable, other methods are available. Anhydrous magnesium perchlorate in various proportions can be dissolved in 72 per cent perchloric acid. Phosphoric anhydride or acetic anhydride may be substituted for the anhydrous magnesium perchlorate.

Significance of Hydrogen Peroxide Decomposition of Perchloric Acid

It is difficult to demonstrate experimentally the formation of hydrogen peroxide by the decomposition of hot, concentrated perchloric acid according to reaction 2, except by interpretation of the resulting effects as shown. Attempts to distill out hydrogen peroxide at a low temperature by passing air through a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid were not successful. Such an experiment using anhydrous perchloric acid might be more successful. If the decomposition products of hot, concentrated perchloric acid do not include hydrogen peroxide, the reactions obtained are exactly analogous to those that would be obtained if hydrogen peroxide or ozone were formed. The odor of ozone was never apparent. The simultaneous formation of hydrogen peroxide and chlorine as decomposition products would be expected to result in side reactions destroying the hydrogen peroxide.

If hydrogen peroxide can be shown to be formed in the reactions of hot, concentrated perchloric acid, or is conceded to have been shown by the studies of the present series of papers, then perchloric acid must be classified as a true per-acid. Present interpretations of the molecular structure of anhydrous perchloric acid and its lower hydrates do not include the assumption of oxygen to oxygen linkages as would be the case if it had true per-acid properties. This question is of far less importance than is the knowledge of the practical influence of the formation of hydrogen peroxide upon the analytical applications.

No violent reactions were encountered in connection with this work.

Summary

Hot, concentrated perchloric acid has been shown to have reducing as well as oxidizing properties. The oxidation reactions result from the decomposition to form chlorine and oxygen. The reducing properties are assumed to result from the simultaneous formation of hydrogen peroxide. An experimental demonstration of its reducing properties has been made.

The reducing reactions of hot, concentrated perchloric acid increase directly with the concentration and temperature. The conditions can be adjusted over a wide range by the use of mixtures of sulfuric acid and perchloric acid and by working at different temperatures. A proper balance between oxidation and reduction relationships can then be obtained.

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Viscosity of Petroleum Products

Methods and Apparatus for Viscosity Measurement

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The probable sources of error encountered in viscometry practice are discussed and methods for eliminating or minimizing these effects are given.

Modified Ostwald pipets designed to minimize the probable sources of error have been constructed, many of which have been in satisfactory use for about 2 years. The pipets are of rugged construction and loss due to breakage is negligible.

Viscosity determinations made by various research workers using different apparatus normally check within 0.2 per cent. The pipets require only 5 cc. of liquid for viscosity determinations. Their application to petroleum work and research in general is indicated.

THE measurement of viscosity by means of capillary tubes dates at least as far back as 1839. In that year, Hagen (*5*) published work anticipating the results obtained by Poiseuille which were published in 1846 (*7*). Because of the completeness of Poiseuille's work, the concept of the laws controlling viscometry flow are generally attributed to him. Since that time, the subject of viscosity has been studied by many investigators. The results obtained substantiate those of Poiseuille in general, although various corrections (usually arising from conditions other than viscous flow) have been proposed. These corrections usually involve drainage, liquid head, kinetic energy, end effects, and surface tension.

Results obtained in capillary viscometers are expressed in terms of absolute or kinematic viscosity. In general, the pressure type of capillary viscometer, in which zero change in liquid head occurs, is preferred for determining viscosities in terms of absolute units. Viscometers similar to the Ostwald type (*6*) are generally preferred when the results are to be expressed in terms of kinematic viscosity.

REDUCTION OF ERRORS IN VISCOSITY MEASUREMENTS

Errors resulting from incomplete drainage may be reduced by making the draining surfaces more nearly vertical, increasing the time of drainage, and decreasing the surface-volume ratio. The nearly horizontal surfaces at the top and bottom of most commercial forms of the Ostwald pipet (Figure 1) are to be avoided. Bingham (*1*) states that the ideal shape of the upper bulb is that produced by placing two cones base to base. The time of drainage may be increased for any given viscosity through pipet design by increasing the capillary length, decreasing the capillary diameter, and increasing the volume of liquid. The last factor also serves to decrease the surface-volume ratio which itself decreases the percentage drainage error. Obviously, the drainage error may be eliminated by measuring the volume of the efflux fluid rather than the volume of the inlet fluid. This is difficult to perform experimentally at various temperature levels except by means of the pressure viscometer (*2*, *3*, *8*).

Most errors in liquid head result from uncertain values of the average head if viscosities are calculated from Poiseuille's law. A second source of error arises from the pipets being at various angles from the vertical during different viscosity measurements. This may be avoided to a considerable extent (Figure 2) by placing one bulb directly over the other (*4*). The degree of this probable error for pipets of different design is shown in Table I. A third source of error results unless precaution is taken to fill the pipet each time with exactly the same volume of liquid. The seriousness of this possible source of error is a function of the size of the lower bulb.

TABLE I. EFFECT OF RELATIVE POSITION OF BULBS ON PERMISSIBLE TILT OF VISCOMETER

ANGLE *A*, FIGURE 1[a]	ANGLE *B*, FIGURE 1[b]
0° 0′	2° 34′
2° 30′	1° 04′
5° 0′	37′
10° 0′	19′
15° 0′	13′
20° 0′	09′

[a] Angle between the vertical and the line joining the centers of the two bulbs.
[b] Angle of tilt which produces an error of 0.10 per cent.

Kinetic energy errors may be minimized greatly through the proper choice of capillary length and diameter and volume of liquid employed. Certain corrections of Poiseuille's law involving $\frac{MU^2}{g}$ have been proposed and experimental data on

this effect have been discussed by Grüneisen (*4*). The relation of kinetic energy correction to viscosity and capillary diameter are given in Figure 3, based both on experimental data and values calculated from $\frac{MU^2}{g}$. Errors amounting to 0.1 per cent are on the upper curve, while errors of 1.0 per cent are on the lower curve. Experimental errors of this nature may be reduced considerably by properly designing pipets for specific purposes, and corrections may be eliminated by calibrating the pipets with liquids of known viscosity throughout the anticipated working range.

Figure 1. Commercial Form of Ostwald Pipet

End effects are closely related to those produced by kinetic energy effects. These effects may be reduced to a considerable extent by employing capillaries having trumpet-shaped ends. In general, kinetic energy corrections include end effects and end corrections include kinetic energy effects.

Surface tension affects viscosity measurements whenever the diameters of the upper and lower bulbs vary greatly. Corrections for surface tension effects may be neglected if the pipets are calibrated with liquids having surface tensions approximately equal to those of the liquids whose viscosities are to be determined. For work with petroleum fractions, this procedure is entirely satisfactory since the surface tensions of various types of oils having equal viscosities do not vary appreciably.

Requirements of Viscometer

Any viscometer, regardless of design, should fulfill certain practical requirements. These are as follows:

1. The viscometer should be sufficiently accurate to produce results in terms of relative viscosity within 0.2 per cent.
2. For convenience the time required for determining the viscosity of any liquid should not be less than 200 seconds nor greater than approximately 2000 seconds.
3. Viscosity measurements should avoid manual operation, control, and constant observation.
4. The viscometer should be capable of operating on not more than 5 cc. of liquid.
5. The usefulness of the viscometer should not be limited by temperature.
6. The viscometer should be capable of measuring the viscosity of any product regardless of its viscous characteristics, provided true fluid flow is obtained.
7. The viscometer should be of sufficiently rugged construction so that undue breakage does not occur.

Development of Modified Ostwald Viscometer

A preliminary review of the existing methods for viscosity measurements indicated that precision of measurement with small amounts of liquid could be best attained with instruments employing capillary tubes.

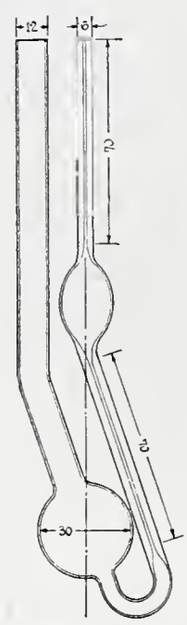

Figure 2. Modified Viscometer Pipet

All dimensions in millimeters.

The Ostwald type of pipet was considered more desirable than the pressure type of capillary viscometer for two reasons: (1) the determination of a great number of viscosities per day required a minimum of complicated apparatus; (2) viscometers of the Ostwald type produce results directly in terms of kinematic viscosity which can be converted readily either into the conventional units of Saybolt viscosity or into units of absolute viscosity.

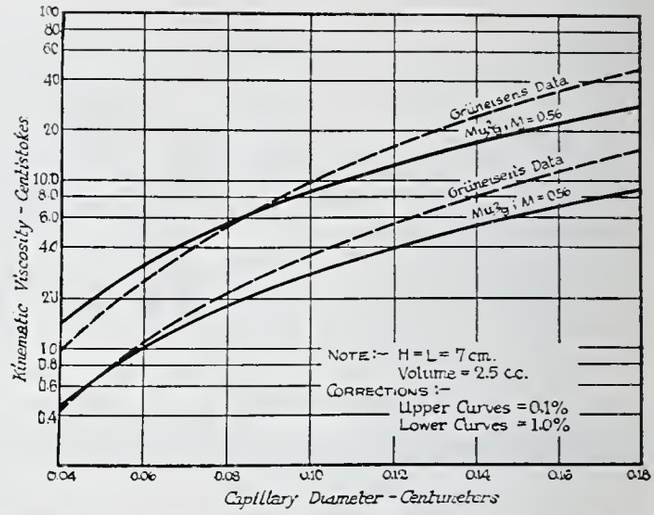

Figure 3. Relation of Kinetic Energy Correction to Viscosity and Capillary Diameter

The modified type of Ostwald pipet (Figure 2) reduces appreciably the first four sources of error, while all five are further minimized by the method of calibration. Drainage errors are reduced by making the upper bulb pear-shaped, assimilating Bingham's recommendation of two cones base to base (*1*). Variations in liquid head are minimized by placing the upper bulb directly over the lower bulb. Kinetic energy corrections are reduced in so far as practical by the proper relation of capillary length to diameter. End effects are minimized by the trumpet-shaped ends of the capillary. Appreciable differences in bulb diameters do not result in significant errors due to surface tension effects.

Table II. Specifications for Three Series of Viscometers

Viscometer series	100	200	300
Total volume required, cc.	5.0	5.0	5.0
Volume of upper bulb, cc.	2.5	2.5	2.5
Diameter of lower bulb, cm.	2.5	2.5	2.5
Capillary length, cm.	7.0	7.0	7.0
Capillary diameter, cm.	0.07	0.12	0.16
Accurate viscosity range (0.1 per cent error)			
Centistokes	4.6–45	40–100	125–1250
Saybolt seconds	41–200	185–1800	560–5500
Useful viscosity range (0.1 to 1.0 per cent error)			
Centistokes	1.4–45	4.0–400	12.5–1250
Saybolt seconds	33–200	39–1800	68–5500

The method of calibrating viscometers is important in the further reduction of errors and in the elimination of correction factors. The generally accepted method for the calibration of viscometers consists in determining the time of efflux for two liquids of known viscosity (the liquids preferably being more viscous and less viscous, respectively, than the anticipated working range) and expressing the calibration of the viscometer in terms of an equation involving two constants and the time of efflux. The equation does not, however, consider other probable sources of error such as drainage, end effects, etc. The fact that calibration by this method is not desirable is indicated by the results shown in Figure 4. The solid curve (temperature = 100° F., 37.8° C.) represents the actual calibration data obtained, while the dotted line represents the results obtained when the calibration curve is calculated from the kinetic energy correction equation and terminal data are employed. It is indicated that there is a possible error of approximately 1 per cent in the pipet constant, and consequently in viscosity.

Corrections for all sources of error other than liquid head

and the negligible effects produced by slight variations in surface tension for oils of equivalent viscosity but of different source and type may be included in the calibration of the viscometer. This is accomplished by calibrating the pipets with several oils of known viscosity which cover not only the maximum and minimum limits of viscosity but also the intermediate range. The time of flow in seconds, divided by the viscosity in stokes or centistokes, is called the pipet constant. A smooth calibration curve results if the pipet constant determined for each different calibrating liquid is plotted against the corresponding time of efflux. A straight line, instead of a curve, usually results if the logarithm of the time of efflux is plotted against the pipet constant. Hence, the correct pipet constant for determining the kinematic viscosity of any unknown liquid is obtained from the plot after the time of efflux for that liquid has been determined. The fact that corrections involving drainage, kinetic energy, end effects, and surface tension (within negligible limits) may be included in the pipet constant is due to the relation of each to the time of efflux. Errors due to differences in surface tension for oils of equal viscosity in pipet of the present design are indicated to be less than 0.05 per cent.

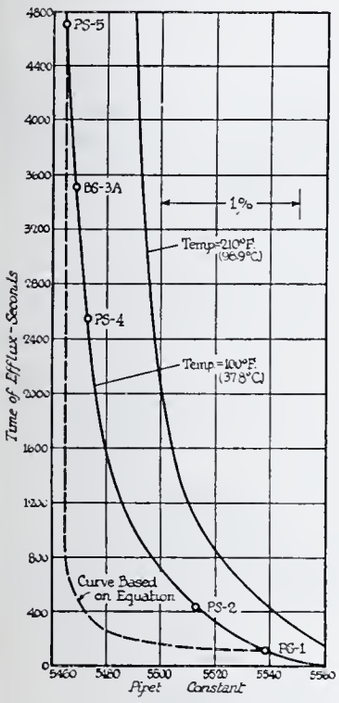

FIGURE 4. CALIBRATION CURVE FOR VISCOMETER 104

Corrections for all major sources of error in viscometry practice other than variations in liquid head are included in the pipet constant by the method of calibration. Significant errors due to variations in liquid head are avoided by filling the pipet with the same amounts of material (either by weighing or more practically by using a volumetric pipet), by placing the upper bulb directly over the lower bulb, and by aligning the pipet vertically within 1° by means of a small plumb-bob.

CONSTRUCTION OF PIPETS

During the past two years, approximately one hundred pipets of the design illustrated in Figure 2 have been made. These pipets have been constructed according to the three classifications of dimensions given in Table II. Series 100 is adapted for determining the 210° F. viscosity of most grades of oil and the 100° F. viscosity of light oils. Series 200 is adapted for determining the 210° F. viscosity of very heavy oils and the 100° F. viscosity of most grades of oil. Series 300 is adapted for determining the 100° F. viscosity of relatively heavy oils.

For viscosity ranges other than those indicated in Table II or for pipets having more particular and specific purposes, reference to Figure 5 will enable capillary diameters to be selected for the case when the capillary length and liquid head is 7 cm. and the volume of liquid flowing through the capillary is 2.5 cc. The middle curve in Figure 5 is based on a minimum time measurement of 200 seconds and the kinetic energy correction data for 0.1 per cent error contained in Figure 3.

Pipets of this design can be fabricated at a reasonable cost.[1] Loss due to breakage is negligible.

ACCESSORY APPARATUS

In making viscosity determinations, the viscometers are supported in water or transparent oil baths which are thermostatically controlled at 100° F. (37.8° C.), 130° F. (54.4° C.), or 210° F. (98.9° C.) within ±0.1° F. A convenient form of thermostat affording complete visibility and low heat loss is shown in Figure 6. Instead of the indicated compressed-air reciprocating motor, an electric motor may be used to drive an efficient stirrer. Cork or rubber stoppers, fitting in the supporting member and slit to facilitate easy removal, serve as suitable supports for the viscometers.

Stopclocks[2] have been found more suitable than stopwatches, since they are of more rugged construction and the minimum times of flow are never less than 200 seconds. Experience with nine stopclocks has led to checking them daily. Changes in room temperature introduce errors in

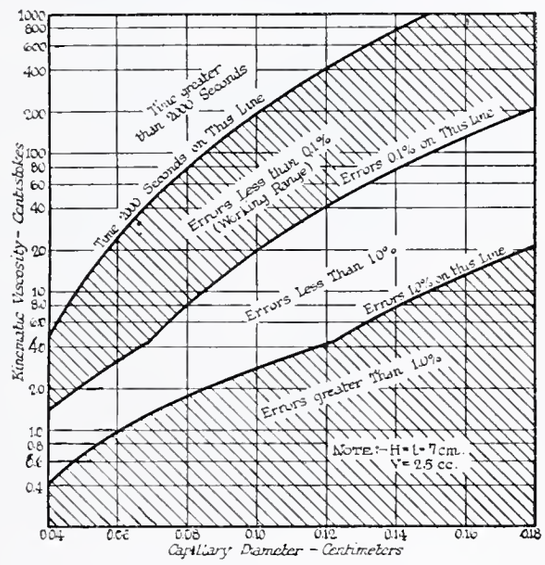

FIGURE 5. CAPILLARY DIAMETERS FOR DIFFERENT VISCOMETERS

measurement of elapsed time, a change from 70° to 90° F. making an error of approximately 0.3 per cent. Also, the clocks should be used only when wound to the same extent.

CALIBRATION OF PIPETS

The method of calibration and the reasons for adopting this method have been given. Satisfactory calibrating liquids may be secured through the Bureau of Standards when the required accuracy is approximately 1 per cent. Especially standardized oils were made in this laboratory for the calibration of the viscometers used. These oils were made from fractions of petroleum having the required viscosity. Prior to standardization, the fractions were treated with anhydrous aluminum chloride, the sludge separated, the oil washed, and then filtered through activated charcoal. Standardization was accomplished by means of a Washburn precision viscometer[3] made of quartz (*9*).

Accurate viscometer constants were obtained by using distilled water as the calibrating liquid at various rates of shear. A value of 1.005 centipoises (1.008 centistokes) was used for the viscosity of water at the calibrating temperature, 20° C. (68° F.).

[1] F. J. Malloy, State College, Pa.
[2] Purchased from Arthur H. Thomas Co., Philadelphia, Pa.
[3] Purchased from the Thermal Syndicate, Brooklyn, N. Y.

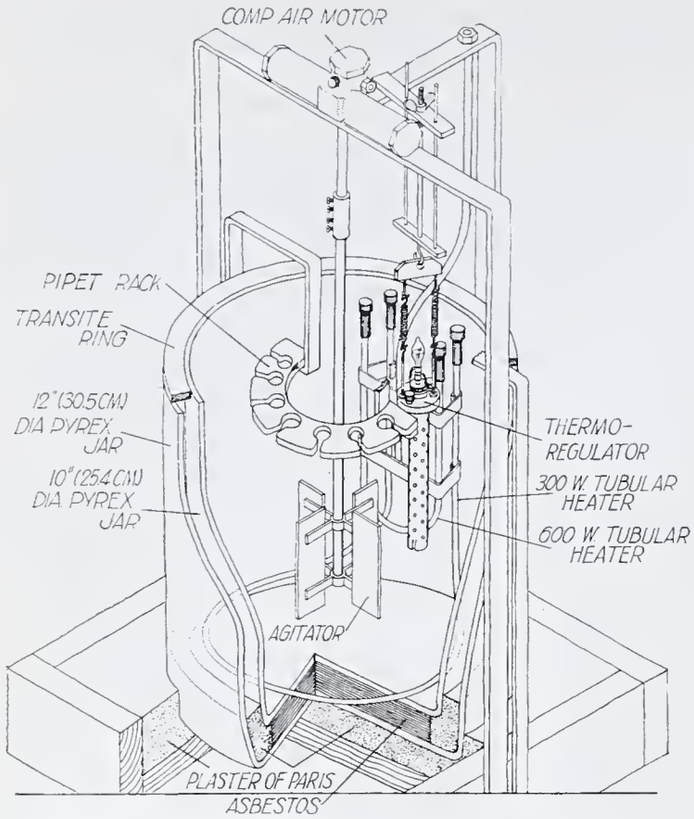

Figure 6. Transparent Constant-Temperature Bath

The viscosities of several different oils, treated as indicated above, were then determined by means of the quartz viscometer. These oils ranged in viscosity at 100° F. (37.8° C.) from 0.0217 to 12.80 stokes (34 to 6200 Saybolt seconds).

Occasionally, standardized oils obtained from the Bureau of Standards were used as an independent check on the calibration. Typical results obtained with two pipets of different series (series 100 and 200) are given in Table III.

Table III. Calibration of Modified Ostwald Viscometers

Standardized Oil	Viscosity of Oil 77° F. (25.0° C.)	Viscosity of Oil 100° F. (37.8° C.)	Pipet 104 Time of efflux	Pipet 104 Pipet constant	Pipet 220 Time of efflux	Pipet 220 Pipet constant
	Centistokes		*Seconds*		*Seconds*	
PS 1		2.170	120.1	55.35		
PS 2		8.010	441.3	55.13	29.7	3.722
PS 4		46.53	2546	54.73	172.3	3.703
BS 3A	64.43		3519	54.69	236.8	3.680
PS 5		86.04	4704	54.65	316.3	3.675
PS 6		157.4			579.7	3.681
BS 5	295.3				1088	3.688
PS 7		398.6			1469	3.684
PS 8		1280			4713	3.681

All viscometers were calibrated at 100° F. Experience has shown that the same calibration data may be used for evaluating the pipet constant at 210° F., provided the change in volume of the oil with temperature, resulting in a change in liquid head, is considered. Calculations indicated that the thermal expansion of Pyrex glass between the limits of 100° F. and 210° F. was negligible in its effect on the viscometer. Actual tests showed this to be true.

Practical Operation

Thousands of viscosity determinations have been made at 100° F. (37.8° C.), 130° F. (54.4° C.), and 210° F. (98.9° C.) during the past two years with pipets of this design. Some twenty research workers have used the pipets successfully. It has been found that different operators using different apparatus can check viscosities within 0.2 per cent. Pipets of this modified design are being used by four other petroleum laboratories.

The time required for making accurate viscosity determinations with these pipets is not excessive. During a recent research program it became necessary to determine approximately 4000 viscosities accurately. One research worker averaged 40 viscosities per day.

These viscometers fulfill the practical requirements listed above.

Acknowledgment

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Use of Solid Carbon Dioxide in the Determination of Tin

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The use of solid carbon dioxide as the source of carbon dioxide gas and as a cooling medium facilitates the determination of tin or the weight of coating on tin plate, by reducing the time required, and by reducing the amount of work required for the determination.

The standard volumetric methods for tin or tin plate require extensive equipment, such as Sellers apparatus, a cylinder of carbon dioxide, and a cooling arrangement where a large number of tin determinations are made. In some laboratories a generator is arranged so that the gases evolved by the dissolving tin can be conducted into a solution of sodium bicarbonate when only a small number of determinations are made at a time. The use of solid carbon dioxide makes it possible to determine tin or the weight of coating on tin plate by using an Erlenmeyer flask, a small watch glass, and a hot plate. No time is required to set up or take down apparatus and any number of determinations can be made at a time. There is no need for a cooling arrangement other than the solid carbon dioxide and the use of solid carbon dioxide reduces the time required for cooling.

The start of the determination is conducted as heretofore up to the point where carbon dioxide is to be passed through the solution. At this point, approximately 0.5 cubic inch of solid carbon dioxide is added to the flask. If it is desired to speed up the work, this may even be crushed into smaller particles. Cooling and purging of the solution take place simultaneously and titration may be commenced when the solid carbon dioxide has about disappeared.

Received February 20, 1934.

Analysis of Gaseous Hydrocarbons

A Method for Determining Gaseous Paraffins and Olefins

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A method of hydrocarbon analysis is described, in which by fractional condensation small samples (500 cc. or less) of complex mixtures are separated into composite fractions containing both two and three, and both three and four carbon atoms per molecule. Density determinations of these composite fractions containing paraffins and olefins and the same fractions after the removal of the olefins, by means of a Stock electromagnetic gas-density balance, give data from which the percentage of each hydrocarbon is readily derived.

Pentane and hydrocarbons of higher molecular weight (gasoline) are determined in the same fractionation.

The accuracy of the method has been verified by the analysis of carefully prepared synthetic mixtures of known composition and application made to the analysis of various types of refinery gases. The method is rapid and of low cost of operation and maintenance.

The work of previous investigators on the analysis of gaseous hydrocarbon mixtures has been summarized in a review (*8*). This study has shown that specific tests are not generally available for the direct determination of individual hydrocarbons in complex mixtures, and that resort must be made to fractional distillation analysis rather than to difference in their chemical behavior.

A precise separation of the individual hydrocarbons in not too complex mixtures can be obtained by means of a fractionating column which utilizes vapor-liquid contact, but the unavoidable hold-up of material in the column makes it necessary to have a sample sufficiently large, usually not less than 4 or 5 liters, to make an error from that source negligible. For the same reason the separation of a very small fraction in a large sample is unsatisfactory. With even the most precise fractionating column, the separation of the individual hydrocarbons in the complex C-4 fraction of highly cracked gases is difficult and time-consuming.

The object of this work was to modify and improve the fractional condensation method of Tropsch and Dittrich (*7*) to a general method for the analysis of mixtures of gaseous paraffin and olefin hydrocarbons, the method being rapid, accurate for the determination of very small samples (less than 0.5 liter of gas), of low cost of operation and maintenance, and suitable primarily for routine analyses in which the composition as ethane, ethylene, propane, propene, butanes, butenes, and pentane and heavier is rapidly determined.

The boiling points of the gaseous hydrocarbons, particularly the simpler ones, depend chiefly upon the number of carbon atoms per molecule and are affected little by differences in structure and unsaturation. For this reason a complex mixture can be more easily separated into fractions containing molecules of the same number of carbon atoms, and with even less difficulty into fractions containing molecules of two and three, and three and four carbon atoms, which can be analyzed by chemical means or by a combination of chemical and physical methods. The latter procedure constitutes the most favorable method for meeting the object of the research.

The mixture of hydrocarbons condensed from the sample at the temperature of liquid nitrogen is distilled into composite fractions containing both two and three, and both three and four carbon atoms per molecule. This fractionation is accomplished without the use of a fractionating column by simple evaporation at controlled low temperatures and correspondingly low pressures and by fractional condensation in a series of glass bulbs cooled to suitable temperatures by liquid nitrogen and by aluminum blocks cooled by this medium. Advantage is taken of the high vapor pressure ratios between the constituents at low temperatures and hence the rates of evaporation, which make possible the selection of temperatures such that the less volatile components present possess in each case a negligible vapor pressure and the more volatile components relatively high vapor pressures. Since these distillation, or condensation, temperatures are maintained fairly constant for the removal of each fraction, the fractionation is effected by varying the pressure rather than the temperature. Very low pressures are employed, 1 mm. or less, which involve correspondingly low temperatures. Two desired advantages accrue from these conditions. The first, and by far the more important, is that the ratio of the vapor pressure of the more volatile component to that of the less volatile component becomes very much greater at low temperatures, and so the separation is distinctly sharper.

Figure 1 shows the per cent ratios of the vapor pressures of hydrocarbons in pairs, curve 1 being the per cent ratio of the vapor pressure of ethane to the vapor pressure of methane at the same temperature. This per cent ratio is not in general the per cent of the more volatile hydrocarbon in the vapor but merely a comparison of the vapor pressures of two hydrocarbons. However, when the two hydrocarbons are present in equal molal proportions in the liquid, the curves do represent the per cent of the less volatile hydrocarbon in the vapor above the liquid and may be interpreted on this basis.

In the first place, the proportion of the less volatile hydrocarbon in the vapor above the liquid increases with temperature in almost a straight-line function. Therefore, the separation of hydrocarbons by fractional condensation improves as the temperature and therefore the pressure are lowered. The curves also give a measure of how the efficiency of separation will change upon a change in temperature.

At a temperature of −100° C., the vapor above a binary mixture of butane and propane of equal molar proportions will contain about 92 per cent of propane, while at a temperature of 0° C. it will contain only about 78 per cent of propane. At very low temperatures the separation is particularly effective in the case of ethane and butane, curve 3, whereas at −100° C. there is only 0.5 per cent of butane in the vapor above a 50-50 per cent mixture. The effect of low temperatures on the ratios is even more pronounced in the case of methane and ethane, curve 1, where at −160° C. there is only about 0.1 per cent of ethane in the vapor above a 50-50 per cent mixture. While the separation of heavier hydrocarbons is not nearly as efficient at correspondingly low temperatures, the trend of the curves indicates that their separation can be made fairly complete by going to very low temperatures.

A second advantage in using very low pressures lies in the fact that the actual amount of the vapor phase over the liquid phase is quite small at the low pressures, and consequently a negligible amount of the vapor phase remains above the liquid at the completion of each distillation, an important consideration where small amounts of gas are used.

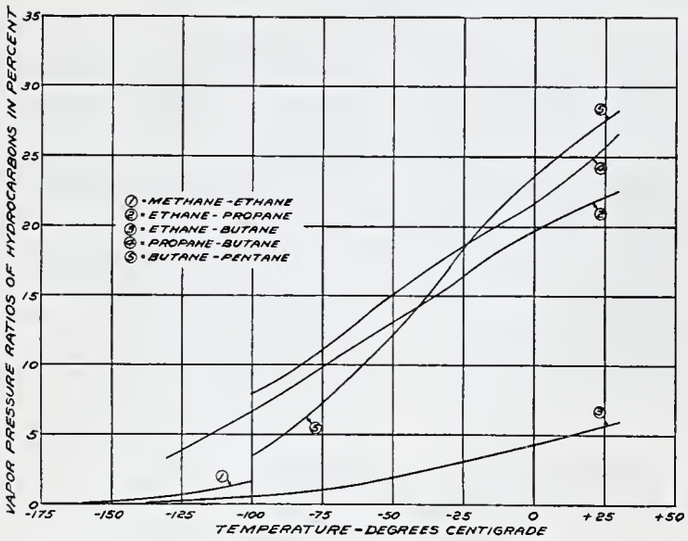

Figure 1. Per Cent Ratios of Hydrocarbon Vapor Pressures

A number of distillations made in this way would be required to obtain results equal to those from one fractionation in a well-designed column. However, the separation into the above composite fractions may be accomplished in one distillation, as it is necessary only to avoid a separation so imperfect as to allow ternary fractions.

In an earlier method of the same type (*1, 7*), the most difficult part of the analysis was the analysis of the composite fractions, which may contain as many as four constituents, two paraffins and two olefins. For a simple gas, such as a natural gas containing only the paraffin hydrocarbons, the procedure would be simple, as no fraction would contain more than two constituents, and the measurement of a single physical property, such as density, thermal conductivity, or refractive index by the interferometer, would serve to determine both. However, if the method is to be general, it must be suitable for the analysis of mixtures which may contain any or all of the following gases: hydrogen, carbon monoxide, oxygen, nitrogen, methane, ethane, ethylene, propane, propene, butanes, butenes, and pentane and heavier. The method described has been developed so as to be suitable for the analysis of the hydrocarbon constituents in such complex mixtures.

The hydrogen, carbon monoxide, oxygen, nitrogen, and methane are easily and rapidly removed from the condensable hydrocarbons at the temperature of liquid nitrogen by reducing the pressure to 0.1 mm. or less, and the percentage of each constituent may be obtained by an Orsat analysis on this fraction. Acetylene is removed from the gas before the condensation is made. The vapor pressure of ethane always remains so low at the temperature of liquid nitrogen (−195° C.) that none of it is removed with the last methane distillates. Pentane and heavier hydrocarbons present in the gas mixture are quantitatively condensed from the butanes and the other gaseous hydrocarbons at a temperature of −105° C. and 1 mm. pressure. The fractionation of the remaining hydrocarbons into two composite fractions is made at 1 mm. pressure and at temperatures of −135° to −140° C. and at −195° C.[1] The components of the fractions are as follows:

Fraction	Temp. of Condensation ° C.	Constituents
1	−195	Ethane, ethylene, propane, propene
2	−135 to −140	Propane, propene, butane, butene
3	−105	Pentane and higher (gasoline)

The analysis of fractions 1 and 2 is made by density determinations, one on the mixture of paraffins and olefins and a second on the paraffins after the removal of the olefins by concentrated sulfuric acid activated by nickel and silver sulfates. From the change in the density of the fraction on the removal of the olefins the density of these olefins is calculated. Then from the density of the two olefins, the density of the two paraffins, the volume of the olefins, and the volume of the paraffins in the fraction, the volume of each hydrocarbon and the volume per cent of each hydrocarbon in the original sample are calculated.

Fraction 3, consisting of pentane and higher hydrocarbons, is reported as gasoline, since these hydrocarbons are liquids at temperatures below 20° C., either as grams per liter of gas, as volume per cent, or as gallons of gasoline per 1000 cubic feet of gas, each of the calculations being made from the volume and the density of the vaporized fraction. Tables have been prepared for facilitating the evaluation of the specific gravity of the gasoline fraction, and by means of a simple relation the gallons of gasoline per 1000 cubic feet of gas may be calculated.

The density determinations are made with a Stock electromagnetic gas-density balance which permits a determination accurate to 3 parts per 1000 in approximately 2 to 3 minutes. This apparatus has been fully standardized and described by Stock and his co-workers (*3–6*).

The gas volumes are determined from the pressure exerted in a known volume of the apparatus at a definite temperature.

Description of Apparatus

Figure 2 shows apparatus for the separation of the liquefied gas sample into fractions by fractional condensation at regulated low temperatures and a Stock electromagnetic gas-density balance for determining the specific gravities or molecular weights of the fractions.

The apparatus for the fractional condensation of the gaseous hydrocarbons consists essentially of five U-tubes, *B, C, D, E,* and *F,* which can be cooled to suitable temperatures by liquid nitrogen and by aluminum blocks cooled by liquid nitrogen; an absorption pipet, *V,* for removing olefins from the fractions; calibrated bulbs, *P, Q,* and *R* for volume measurements; and a manometer, *Y,* for pressure readings. The temperature of the aluminum block is indicated by means of an iron-constantan thermocouple calibrated at the freezing points of water, mercury, and carbon disulfide, and at the boiling point of liquid nitrogen. The junctions of the iron and the constantan wires with the copper lead wires from the millivoltmeter are maintained at a constant temperature of 100° C. by immersion in steam.

The soda-lime tube and anhydrone drying tubes are constructed so as to eliminate all rubber connections or stoppers and to permit their easy removal for cleaning and refilling. Anhydrone, magnesium perchlorate, is used as the drying agent rather than phosphorus pentoxide, which has been found to remove olefins after it has absorbed some moisture.

The precision manometer, *Y,* permits pressure readings from 0 to 800 mm. of mercury, made accurate to 0.2 mm. by use of a mirror scale and 25-mm. tubing to overcome capillary attraction. The manometer is a modification of the one described by Germann (*2*) improved for the authors' purposes.

The construction of the aluminum blocks *I* and *J* used in cooling the condensation tubes is shown in detail in Figure 3. Table I shows the approximate rate of cooling, rate of heating, and the amount of liquid nitrogen used in cooling the blocks.

[1] These temperatures are slightly lower than those used by Tropsch and Dittrich, but more suitable for the condensation as shown under Selection of Temperatures for Condensations.

Table I. Cooling and Heating Rates of Aluminum Blocks

	° C.	° C./min.	Volume of Nitrogen Cc./° C.
Rate of cooling	0 to −80	28	...
Rate of cooling	0 to −100	25–30	...
Rate of heating	−65 to −60	0.2–0.3	...
Rate of heating	−115 to −100	0.9	...
Rate of heating	−130 to −115	0.9	...
Liquid nitrogen required for cooling	0 to −80	...	1.8
Liquid nitrogen required for cooling	0 to −100	...	1.9–2.1

Preliminary cooling with solid carbon dioxide and acetone lowers the temperature to about −80° C., so that less liquid nitrogen is required. The temperatures required for the condensations are maintained by the occasional addition of small amounts of liquid nitrogen. Alcohol is placed in the blocks around the condensation tubes so as to insure more rapid heat transfer.

The first aluminum block used had only one hole for liquid nitrogen, and, especially when the block was warm, the nitrogen boiled so rapidly that considerable quantities were lost in cooling it, and, if the nitrogen was added in such small amounts as to prevent its being wasted, the time required to cool the block was much too long. With the block shown in Figure 3, the liquid nitrogen passes to the bottom of the Dewar flask and boils up through the many small holes in the rim of the block, permitting rapid cooling with no loss of liquid nitrogen.

The calibrated bulbs *P*, *Q*, and *R*, in addition to serving as known volumes for the measurement of the fractions, permit the entire fractions to be transferred to these bulbs, by condensation in *M*, *N*, or *O*, and vaporized so as to obtain a homogeneous mixture before being passed into the gas balance for the molecular weight determination. If the fractions are allowed to vaporize and pass directly into the balance, the lighter components enter the balance first and cause errors in the molecular weight determinations as high as 10 per cent.

The volumes of *P*, *Q*, and *R* are accurately determined before being sealed into the apparatus and are then used to determine the volume of the balance and the manometer, *Y*, since the volume of the balance and the manometer must always be added to any combination of bulbs *P*, *Q*, or *R*. The volume of *P* is approximately 150 cc., *Q* 200 cc., and *R* 500 cc. The volume of the balance, manometer, and connections to stopcocks 6, 10, and 17 is approximately 250 cc.

The activated sulfuric acid is a mixture, in the proportion 1 to 15, of concentrated sulfuric acid (specific gravity 1.84) saturated with nickel sulfate at room temperature, and concentrated sulfuric acid containing 0.6 per cent of silver sulfate (*7*).

The Stock gas-density balance operates according to the principle of determining specific gravity by measuring the Archimedic buoyancy produced on a small hollow quartz ball fastened to a scale beam by the influence of the surrounding gases. The scale beam, into which a thin staff magnet has been fused, bears at the other end a second hollow quartz ball serving as counterbalance which is open and whose total surface is approximately equal to the surface of the buoyancy ball, in order to avoid final one-sided loading by absorption of gases. The balance beam rests on steel points in stone pans and is in a glass case closed with a ground cap and having ground connections for introduction of gases. The glass balance housing is suspended in a glass trough which is filled with a temperature bath. An observation microscope makes possible convenient observation of the fine-

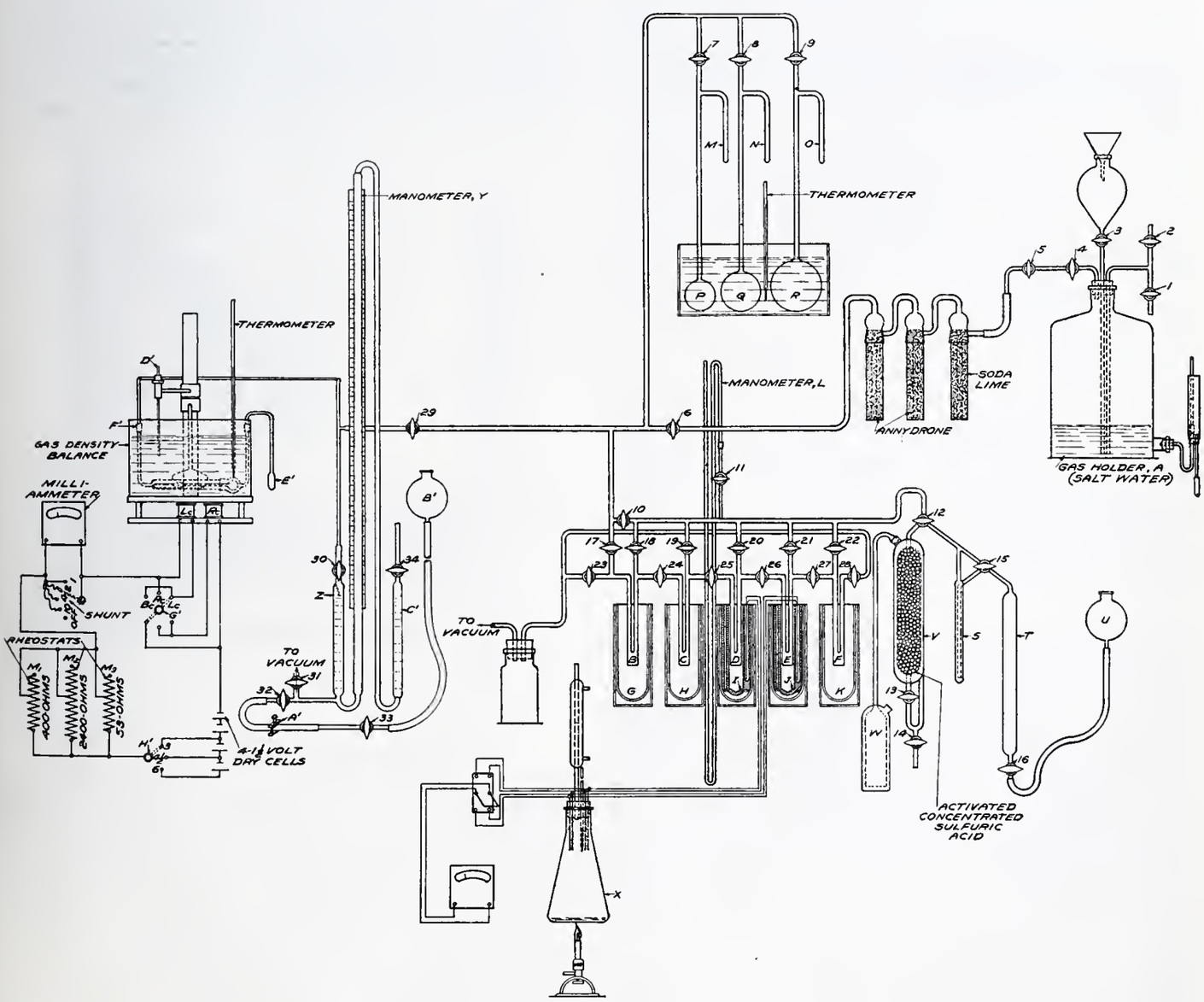

Figure 2. Gas Analysis Apparatus

scale pointer which plays before a fixed counterpointer arranged in the balance frame. Beneath the balance are the electromagnets, *Lc* and *Rc*, free of iron and therefore of hysteresis, for magnetic influencing of the balance.

Water is contained in the bath around the balance and a thermometer indicates the temperature to 0.1° C. The small auxiliary magnet, *D′*, for correcting the zero position of the balance beam (in vacuum) is usually suspended over the center of the balance beam and the adjustments are made by raising or lowering the magnet.

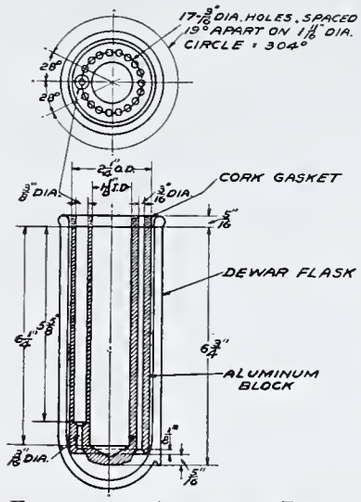

Figure 3. Aluminum Block for Cooling Condensation Tubes

The gas balance is supported on a rigid stand near the manometer and is connected to the manometer and the fractionation apparatus with 8-mm. tubing through a ground-glass joint, *F′*. The arrangement and connection of shunts, resistances, milliammeter, etc., are shown in Figure 2. Switch *G′* permits the left-hand coil, *Lc*, the right-hand coil, *Rc*, or both coils to be used. With the resistances M_1, M_2, and M_3 and the switch *H′*, by which two, three, or four dry cells can be thrown in the circuit, currents from 0.5 to 100 milliamperes can be sent through the coils. The milliammeter reads from 0 to 15 milliamperes with an accuracy of 0.02 milliampere, and three shunts reduce the current by one-half, one-quarter, and one-tenth, so that any current up to 150 milliamperes can be read. The resistance coils, shunts, batteries, and switches are mounted on a Bakelite switchboard and carefully checked against current leakages or short circuits.

In operation, the scale housing is filled with the gas under investigation, whereupon the scale, which balances in a vacuum, is brought out of equilibrium as a result of the bouyancy of the closed quartz bulb. The balance is then again adjusted to zero by sending a current of suitable strength through the electromagnet. From a calibration curve taken previously with dry air, the specific gravity of the gas is derived immediately.

The accuracy of the balance was carefully checked by a large number of determinations on air and on various hydrocarbon gases and was found to average three parts per thousand. The values for the hydrocarbon gases were checked by the Dumas method with the same order of accuracy. The balance operates best in a location free of vibration and one in which all iron bodies are stationary. The presence of iron has no influence, but changes in its location near the balance cause variations in the zero position of the balance.

Procedure

Calibration of Balance. The gas balance is calibrated with dry air free of carbon dioxide. The balance and manometer are evacuated through stopcocks 17, 23, 29, and 30 by means of a Cenco Hyvac pump capable of producing a vacuum of less than 0.001 mm. of mercury. The balance beam is then adjusted to the zero point by raising or lowering the magnet *D′*. Stopcocks 17 and 30 are closed and 6 is opened slowly to allow air to pass slowly through the gas holder, the soda lime, and the anhydrone into the gas balance. Stopcock 29 is then closed and the pressure in the balance determined by carefully opening stopcock 30 and at the same time admitting mercury to the manometer from *B′*. After the mercury level has risen almost to the zero point, *Z*, the final adjustment of the mercury level to the zero point is made with the screw clamp, *A′*. The switch, *G′*, is set on coil *Lc*, and the milliamperes of current necessary just to balance the beam are determined. The milliammeter reading, the temperature of the balance to 0.1° C., the manometer reading to the nearest 0.2 mm., and the temperature of the manometer to the nearest 0.5° C. are recorded. The balance and the manometer are again evacuated by closing stopcocks 6 and 30 and opening 17 and 29. *B′* is lowered, stopcock 33 opened, and, as the mercury level in the manometer falls, stopcock 30 is opened slowly to keep the mercury level near *Z*. When the mercury levels are below *Z* stopcock 33 is closed and 30 opened fully. The evacuation is completed and the operation repeated until at least four determinations have been made for each shunt at pressures distributed over the range of that particular shunt.

The apparent molecular weights, calculated from the temperature and corrected pressure, are plotted as ordinates and the corresponding milliamperes of current as abscissas. The straight line connecting these points should pass through the origin. If the line does not pass through the origin, the zero point has not been properly adjusted.

The Analysis

The sample for the analysis is measured in gas holder *A* over salt water. The volume of the sample is usually 300 to 500 cc., depending upon the noncondensable gases present. The most suitable quantity is about 200 to 300 cc. of hydrocarbons above methane. The sample may also be measured in the calibrated bulbs *P*, *Q*, or *R* from the pressure and temperature.

The sample is admitted slowly to evacuated condensation tubes *B* and *C* which are cooled by immersion in liquid nitrogen contained in Dewar flasks *G* and *H*. If the pressure, indicated by manometer *L* through stopcock 19, reaches atmospheric, the excess of noncondensables is allowed to pass into the vacuum line through stopcock 25, but the pressure in *B* and *C* is kept near atmospheric until all the sample is displaced from the gas holder. The pressure is then lowered slowly to remove noncondensables and gases dissolved in the liquefied hydrocarbons, the last traces of which are removed by distilling the hydrocarbons in *B* into *C* with stopcock 25 open to the vacuum and *C* immersed in liquid

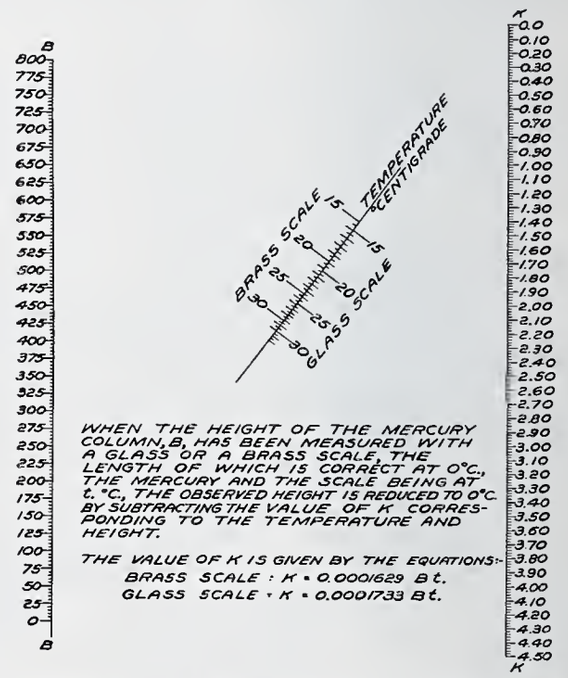

Figure 4. Nomographic Chart for Reduction of Barometer Readings to 0° C.

nitrogen, and then from *C* back into *B* with stopcock 25 closed, 23 open, and *B* immersed in liquid nitrogen. Usually two or three distillations will completely remove methane and dissolved gases.

The condensed sample, contained in *C*, is allowed to vaporize slowly and pass at 1 mm. pressure, indicated by manometer *L*, into condensation tube *D*, cooled to −105° C., tube *E*, cooled to −135° to −140° C., and tube *F*, cooled to −195° C., stopcock 28 remaining open to the vacuum during this distillation. At the end of the distillation, the fractions are closed off in their respective condensation tubes. The aluminum blocks are cooled during the condensation of the sample and the preliminary distillations.

Fraction 1, containing ethane and ethylene and a part of the propane and propene, is distilled to bulb M, N, or O, depending on its volume, allowed to vaporize into P, Q, or R, and then, with stopcocks 10 and 17 closed, admitted to the gas balance and manometer Y for the molecular weight determination. The milliammeter reading, the temperature of the balance, the manometer reading, and the temperature of the manometer are recorded. Stopcock 10 is opened and the gas allowed to pass through stopcock 12 into S, forcing the mercury out of condensation tube S into buret T. Fraction 1 is then condensed in S by cooling in liquid nitrogen. If the pressure is not sufficient to force the mercury from S into T, the fraction is condensed first in F, stopcock 10 closed, and the fraction then vaporized. After the fraction, now in S, is vaporized into T, it is passed into pipet V, the portion in S being displaced by mercury. As soon as the olefins are absorbed, the remaining paraffins, fraction 1-a, are distilled back into M, N, or O, vaporized, and the molecular weight is determined.

The same procedure is applied to fraction 2 which contains the remainder of the propane and propene and the butanes and butenes. The analysis is complete when fraction 3, the gasoline fraction, is distilled to M, vaporized, and the molecular weight determined.

The absorption of the olefins by the activated acid in V usually requires 6 to 9 minutes for fraction 1, and 3 to 6 minutes for fraction 2, and the procedure is arranged so that, while the absorption is being made on fraction 1, the molecular weight of fraction 2 is determined, and, similarly, while the olefins are being absorbed from fraction 2, the molecular weight of fraction 3 is determined. When the data on a fraction are complete, the fraction is removed from the apparatus through stopcock 23 or 28.

About 1.5 to 2 hours and approximately 1 liter of liquid nitrogen are required for an analysis. The operation of the apparatus can be learned by an operator in a short time as a manipulative process without necessity for thorough understanding of the theory involved.

Data and Calculations

A typical set of data is shown in Table II.

Table II. Typical Data Obtained in Analysis of Complex Hydrocarbon Mixture

(Volume of sample, 295.5 cc.)

Fraction	Volume	Molecular Weight
	Cc.	
1	96.0	35.90
1-a	57.3	37.23
2	113.2	52.96
2-a	78.3	54.62
3	35.5	72.47
Noncondensable	50.8	...

The following relations have been derived for calculating the volume of each hydrocarbon constituent in each of the fractions:

Fractions 1 and 1-a. (1) Ethane and propane

$$\text{Volume of ethane} = \left(\frac{45.25 - \text{molecular weight of 1-a}}{14.85}\right) \text{volume of 1-a} \quad (1)$$

$$\text{Volume of propane} = \text{volume of 1-a} - \text{volume of ethane} \quad (2)$$

(2) Ethylene and propene

$$\text{Volume of ethylene} = 3\,(\text{volume of 1} - \text{volume of 1-a}) - \left(\frac{\text{volume 1} \times \text{molecular weight of 1} - \text{volume of 1-a} \times \text{molecular weight of 1-a}}{14.02}\right) \quad (3)$$

$$\text{Volume of propene} = \text{volume of 1} - \text{volume of 1-a} - \text{volume of ethylene} \quad (4)$$

Fractions 2 and 2-a. (1) Propane and butane

$$\text{Volume of propane} = \left(\frac{59.87 - \text{molecular weight of 2-a}}{14.62}\right) \text{volume of 2-a} \quad (5)$$

$$\text{Volume of butane} = \text{volume of 2-a} - \text{volume of propane} \quad (6)$$

(2) Propene and butene

$$\text{Volume of propene} = 4\,(\text{volume of 2} - \text{volume of 2-a}) - \left(\frac{\text{volume of 2} \times \text{molecular weight of 2} - \text{volume of 2-a} \times \text{molecular weight of 2-a}}{14.02}\right) \quad (7)$$

$$\text{Volume of butene} = \text{volume of 2} - \text{volume of 2-a} - \text{volume of propene} \quad (8)$$

With these relations and the data in Table II, the data in Table III are calculated.

Table III. Data Calculated from Molecular Weight and Volume of Fractions

Hydrocarbon	Fraction 1	Fraction 2	Total	Volume Per Cent in Sample
	Cc.	*Cc.*	*Cc.*	
Methane	..	..	50.8	17.2
Ethane	31.0	..	31.0	10.5
Ethylene	22.5	..	22.5	7.6
Propane	26.3	28.1	54.4	18.4
Propene	16.2	17.1	33.3	11.3
Butanes	..	50.2	50.2	17.0
Butenes	..	17.8	17.8	6.0
Pentane	..	..	35.5	12.0

The volume per cent of each hydrocarbon in the original mixture is calculated from the volumes derived through the above relations and the volume of the original sample, the volumes of propane and of propene being the sum of the volumes of these hydrocarbons in fractions 1 and 2.

The per cent of methane plus noncondensable gases is calculated from the difference in the volume of the sample and the sum of the volumes of fractions 1, 2, and 3.

Since the molar volumes of the gaseous hydrocarbons, especially the paraffins, vary considerably from that of an ideal gas, the molecular weights or rather the weight (grams) of 22.41 liters have been calculated from the experimentally determined densities. Complete data have not been found in the literature for the olefins. The data for the paraffin hydrocarbons are shown in Table IV.

Table IV. Experimentally Determined Densities of Paraffin Hydrocarbons

Hydrocarbon	Weight: 1 liter	Weight: 22.41 liters
	Grams	*Grams*
Ethane	1.3564	30.40
Propane	2.0190	45.25
n-Butane	2.6753	59.95
Isobutane	2.6678	59.79

It is clear that the molar volumes of the hydrocarbon gases would reach the theoretical values at zero pressure, but at the pressures used in the authors' experiments the deviation was not appreciably influenced by pressure and they could use the values in Table IV with better results than could be obtained by using the theoretical values.

Since the value given in the literature for the density of ethylene (1.2604 grams per liter) is close to the calculated and the value obtained by the authors on the Stock gas-density balance (2.529 grams per liter) for isobutene is also so close to the calculated value as not to cause any appreciable error in the calculations, the theoretical values have been used for the olefins.

Normal and isobutane are determined together in this analysis, and the average weight of 22.41 liters of these hydrocarbons, 59.87, has been used as the value for butane.

For the calibration of the balance, the apparent molecular weight, M, of air is calculated from the pressure and temperature corresponding to a particular current by the following relation:

$$M = 28.98 \times \frac{P}{760} \times \frac{273}{t + 273}$$

The apparent molecular weight, M, read from the calibration curve, molecular weight–milliampere relation, is

calculated to the molecular weight at 0° C. and 760 mm., M_0, by the relation,

$$M_0 = M \times \frac{760}{P} \times \frac{t + 273}{273}$$

All pressure readings are reduced to 0° C. since at pressures over 100 mm. the expansion of the mercury introduces an appreciable error in the readings. A nomographic chart, Figure 4, has been constructed from which corrections between 15° and 32° C. and to 800 mm. pressure can be read directly.

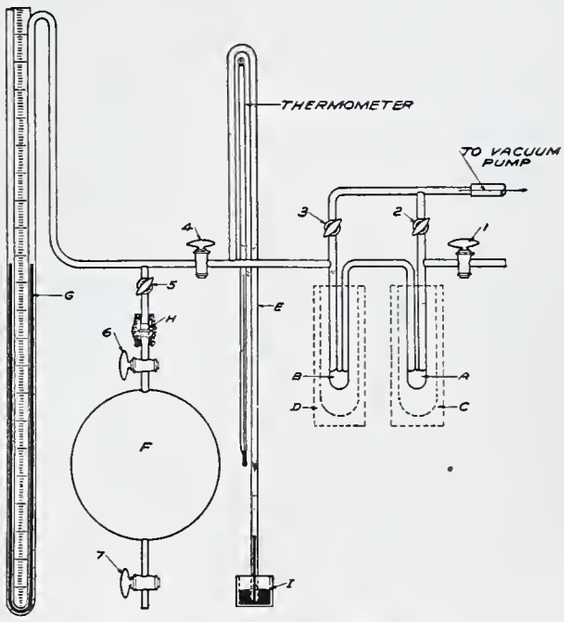

Figure 5. Apparatus for Preparation of Synthetic Gas Mixtures

The volumes of the fractions are calculated from the pressures as read on Y to 0.2 mm., the temperature of the bulbs P, Q, and R to 0.1° C., and the known volume of the apparatus.

Selection of Temperatures for Condensations

The quantitative separation of methane from C-2 hydrocarbons at the temperature of liquid nitrogen (−195° C.) has been well established by a number of investigators, and in this work it has been found unnecessary to provide for the possibility of the presence of C-2 hydrocarbons in the methane fraction.

An inspection of low-temperature vapor pressure data of the gaseous hydrocarbons indicates that at a temperature between −120° and −150° C. the C-4 hydrocarbons should, at pressures of 1 mm. or less, be quantitatively condensed from C-2 hydrocarbons, and similarly, pentanes and heavier from C-4 hydrocarbons at temperatures between −90° and −110° C.

To determine the temperature most suitable for the quantitative separation of C-2 and C-4 hydrocarbons, synthetic mixtures of ethane and isobutane of known composition were fractionated at temperatures between −120° and −160° C. Isobutane was taken for this separation rather than n-butane, since isobutane, owing to its lower boiling point, is more difficult to separate. At temperatures between −135° and −140° C. the separation of isobutane from ethane was quantitative. In addition to the measurement of the gas volumes from the fractionation and their comparison with the calculated values, the purity of the fractions was verified by accurate molecular weight determinations. With 50 per cent mixtures, no ethane was condensed at temperatures between −120° and −140° C.; 0.08 per cent was condensed at −145°, 1.2 per cent at −150°, 1.7 per cent at −155°, and 3.1 per cent at −160° C. Similar results were obtained with other ethane-butane mixtures of varying composition.

In similar experiments with n-butane–pentane mixtures, the condensation of pentane was −99.1 to 99.7 per cent complete at −100° C. and 100 per cent at −105° C. Accurate molecular weight determinations showed that no butane was present in the pentane fraction. With mixtures containing over about 5 per cent of butanes, a small amount of butane was condensed in the fractionation but was completely removed by a second distillation.

Accuracy of Method

The analysis of a number of complex synthetic hydrocarbon gas mixtures of known composition has shown the method to give values of a high order of accuracy.

The Podbielniak fractionating column was used in the purification of the gaseous paraffin and olefin hydrocarbons. Samples of ethane, ethylene, propane, propene, n-butane, and isobutane were obtained from cylinders of the compressed gases and fractionated on the column until a constant-boiling fraction was obtained. Isobutene was prepared from tertiary butyl alcohol and oxalic acid and 1-butene from n-butyl alcohol by dehydration over alumina. These butenes were also purified by fractionation on the Podbielniak column.

The apparatus used in the preparation of synthetic gas mixtures is shown in Figure 5. The entire apparatus, including the 5-liter bulb, F, was evacuated through stopcocks 2 and 3; stopcock 4 was then closed. The hydrocarbon was admitted through stopcock 1 and condensed in bulb A which was cooled in liquid nitrogen contained in Dewar flask C. Stopcock 1 was then closed and 3 opened to the vacuum, to remove any air that may have contaminated the sample during storage or in being transferred. Any dissolved air was removed by distilling the hydrocarbons into B, which was cooled in liquid nitrogen contained in D.

The condensed gas, now contained in B, was transferred to F by closing stopcock 3 and lowering D until the pressure in B was near atmospheric, as indicated by manometer E. Stopcock 4 was then opened carefully until the pressure, as shown by manometer G, indicated that the desired amount of the hydrocarbon had been admitted to F. The excess was allowed to vaporize and pass out through stopcock 1 or was removed through the vacuum pump. The absolute pressure of the gases in F was obtained by subtracting the difference in the mercury levels of manometer G from the atmospheric pressure. The volume per cent of each gas was calculated by dividing the pressure exerted by each gas by the total pressure of the mixture, all pressure readings being reduced to 0° C. F was removed from the apparatus through ground joint H and the mixture displaced by mercury or salt water.

This method of preparation of synthetic gas mixtures is rapid and accurate, and excludes the possibility of contamination by air or of any absorption of the gases by salt water, as is usually experienced in other methods for the preparation of these mixtures.

The analysis of one of the synthetic mixtures prepared in this manner is shown in Table V.

Table V. Analysis of Synthetic Mixture

Hydrocarbon	Volume Per Cent of Condensation Analysis 1	2	Av.	Calculated Volume %
Methane + air	21.6	21.5	21.6	21.8
Ethane	10.5	10.4	10.5	12.1
Ethylene	10.7	9.7	10.2	10.5
Propane	14.0	15.9	15.0	15.1
Propene	11.7	11.8	11.8	10.9
Isobutane	15.7	14.5	15.1	4.0
n-Butane				10.2
Butenes	10.6	10.7	10.7	10.0
Pentane	5.4	5.4	5.4	5.5

Isobutane and n-butane are reported as total butanes, so the values given for n-butane correspond to the calculated value of 14.2 per cent.

The method has been applied to the analysis of a number of refinery gases. Typical examples are shown in Table VI.

TABLE VI. ANALYSIS OF REFINERY GASES

Hydrocarbon	Sample 1	Sample 2	Sample 3	Sample 4
Methane + air	0.1	14.8	0.0	0.0
Ethane	3.3	2.5	2.8	4.8
Ethylene	0.2	0.0	1.4	0.0
Propane	24.2	27.1	36.4	30.8
Propene	10.7	0.0	11.1	15.9
Butanes	33.6	52.1	24.6	33.0
Butenes	26.6	0.0	28.7	11.7
Pentane +	1.5	3.5	0.0	3.8

ADVANTAGES OF METHOD

The chief advantages of this method lie in its application to the complete accurate analysis of small samples, less than 0.5 liter, the rapid, routine analysis of all types of gases, and the low cost of apparatus and of operation.

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Estimation of Aldehydes in Rancid Fats

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Statements in the literature suggest that aliphatic aldehydes of medium molecular weight, in particular heptaldehyde and nonaldehyde, are the compounds mainly responsible for the objectionable odor and flavor of oxidized fats.

An investigation of the bisulfite method has therefore been carried out with a view to estimating small quantities of these substances in solution in an oil or fat. Purified heptaldehyde has been employed and the sensitivity of the method increased until the aldehyde content of 1 gram of cottonseed oil (containing approximately 0.1 per cent of the aldehyde) can be determined with an accuracy of the order of 0.001 per cent.

Specimen data are given on the development of aldehydes in oxidizing fats.

THOUGH the theories which have been proposed from time to time to account for the deterioration produced in fats by autoxidation of the unsaturated constituents differ in detail, they all agree in postulating that the first stage in the reaction consists in the addition of molecular oxygen to the double bonds of the unsaturated acids with production of labile peroxides which then further isomerize, decompose spontaneously into, or react with water to form a complex series of products including aldehydes, ketones, and acids of lower molecular weight.

CHEMICAL TESTS FOR RANCIDITY

Various chemical methods based upon the presence of one or other of the above-mentioned decomposition products have been suggested for the detection and estimation of rancidity, of which the peroxide and Kreis tests, and in smaller degree the Schiff and Issoglio tests, are probably the best known.

The peroxide estimation (*11*) has proved itself of particular value in investigating the earliest stages of the oxidation of fats, its sensitivity making possible an investigation of those slow changes during the induction period which lead to rapid oxidation and the accompanying deterioration in odor and flavor. In some cases the peroxide test has been successfully applied in the presence of protein (*10*), thus avoiding the very real difficulty of extracting the fat unchanged from the tissue. In recent work determination of peroxide oxygen appears also to be displacing other less reliable or more cumbersome methods in heat-accelerated tests for the determination of relative susceptibility to oxidation (*9*, *17*).

The Kreis reaction, stated by Powick (*13*) to be due to the presence in the fat of a derivative (possibly a glyceryl acetal) of epihydrin aldehyde, has been widely used as a criterion of oxidation rancidity but has recently been adversely criticized in America and in Germany by committees set up to investigate it.

The Schiff test with fuchsin–sulfurous acid for the aldehyde grouping has been applied to the detection of rancidity in fats by Browne (*3*), Fellenberg (*7*), and others, but always in a qualitative or at best a very rough quantitative manner; while determination of the permanganate-reducing power of the steam-volatile or water-soluble products obtainable from a known weight of oil under standard conditions has also found some practical application but is rather empirical in nature.

Much controversy has occurred in the past as to the ability of the various chemical tests to parallel rancidity as judged by odor and flavor. Actually, as Barnicoat (*1*) has recently pointed out in case of the Kreis and peroxide tests, there are no values above which oils and fats in general are invariably rancid and below which they are sweet. The points on the peroxide-oxygen and Kreis curves at which a fat becomes perceptibly rancid depend on the nature of the fat (generally speaking, a low content of acids less saturated than oleic favors the early development of rancidity but this generalization holds better for normal than for high temperatures), and also in some degree on the conditions of temperature and light to which it has been subjected. It has, for example, already been shown (*1*, *11*) that the ratio between the rates of peroxide accumulation and development of the Kreis reaction is not constant for a particular fat, but increases with falling and decreases with rising temperature—a result probably attributable to a greater stability of the peroxide at lower temperatures. Similarly the ratio between the observed peroxide and Kreis values is not the same for different oils under similar conditions.

In view of the wide variation in sensitivity to "off" odors and flavors displayed by different individuals, and by the same person at different times, and of the difficulty of fixing standards for odor and flavor, a quantitative chemical test which would correspond more closely to the organoleptic method than do the existing ones would clearly be of considerable value. Such a result would, of course, best be achieved by estimating directly the substance or substances actually responsible for the rancid odor and flavor.

Tests for Aldehydes

Among the products of the atmospheric oxidation of fats the aliphatic aldehydes of medium molecular weight immediately stand out as possible sources of the deterioration in odor and flavor, and Scala (*15*) as far back as 1908 expressed the opinion that heptaldehyde and nonaldehyde, and to a smaller extent hexaldehyde and butaldehyde, are actually the substances concerned. More recently Powick (*13*), as the

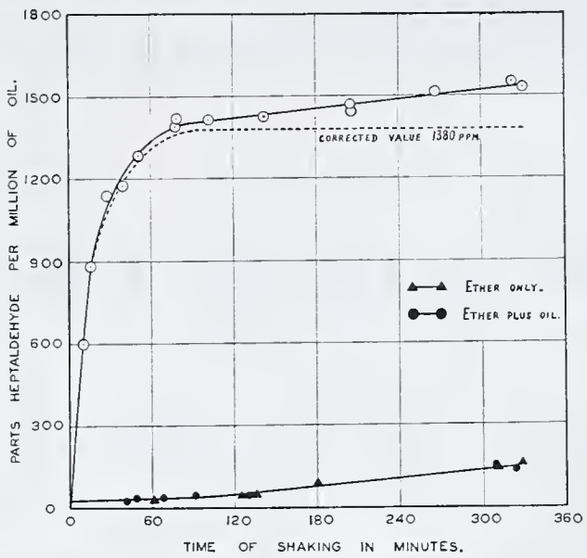

Figure 1. Estimation of Heptaldehyde in Cottonseed Oil by Direct Titration Method, Using Ether and 0.1 *N* Sodium Bisulfite

result of an examination of a large series of the compounds which might reasonably be present in an oxidized fat, came to the conclusion that of these only heptaldehyde, and in a smaller degree nonaldehyde, could contribute appreciably to the rancid odor. On the basis of these results it was decided to attempt the estimation of the minute amounts of aldehydes present in oxidized fats.

The Schiff Test. A series of experiments was therefore carried out with the object of placing the Schiff reaction on a quantitative basis, but neither by Fellenberg's (*7*) technic nor by various modifications of it could quantitative results be obtained. The color produced in the test often appeared to concentrate at the interface between the two phases and attempts to carry out the reaction in a single-phase medium by means of alcohol or glacial acetic acid were not successful. Schibstead (*16*), however, in a paper which has appeared since the above work was carried out, has succeeded in obtaining quantitative results from a modification of the Schiff test. According to this author's technic the fat in petroleum ether solution is shaken with a solution of rosaniline hydrochloride–sulfurous acid in 50 per cent alcohol (which is red), and the color produced in the petroleum ether layer compared with a cresol red standard at pH 8.3. The actual depth of color obtained from a given specimen of fat is dependent upon the concentrations of alcohol, sulfur dioxide, and hydrochloric acid employed, on the proportion of reagent to fat solution, and on the shape of container, manner of shaking, and time and conditions of standing; all of these variables being adjusted so far as possible for maximum color development. Simple aldehydes such as heptaldehyde do not develop any color in the petroleum ether phase, the test apparently being specific for aldehydes of high molecular weight whose condensation products with rosaniline hydrochloride are soluble in petroleum ether. The substances reacting in rancid fats are therefore presumably the glyceride-aldehyde residues which remain after splitting off of the simple aldehydes. Schibstead also states that samples of oleic and linoleic acids which had quite a tallowy odor failed to give any reaction with the reagent.

The Bisulfite Method. As an alternative to the Schiff reagent the bisulfite method for the estimation of aldehydes seemed to offer the best hope of success. Ripper's original method (*14*) improved by Clausen (*4*) has already been used by Clausen and by Friedemann, Cotonio, and Schaffer (*8*) to estimate small amounts of acetaldehyde produced by oxidation of the lactic acid present in tissues, and by Clift and Cook (*5*) for the determination of pyruvic acid and other carbonyl-containing compounds in samples of biological origin. Briefly, the method consists in allowing the solution containing the aldehyde to react with a solution of sodium bisulfite. The excess of the latter is then destroyed by addition of iodine, sodium bicarbonate is added to facilitate dissociation of the aldehyde bisulfite compound, and the combined bisulfite is titrated with standard iodine.

For use with fats the main practical difficulty, apart from the extremely small quantities involved, is that of securing adequate contact between the aqueous reagent and the fat in order that complete extraction may be obtained.

Estimation of Heptaldehyde

As experimental material solutions of heptaldehyde of known concentrations were made up in the solvent under investigation or in freshly refined cottonseed oil. The commercial product usually analyzed to about 70 to 90 per cent heptaldehyde and was purified via the bisulfite compound before use.

Two or three of the samples thus prepared displayed a rather remarkable instability, the liquid after two or three days becoming turbid through separation of water (?) and of fine needle-like crystals resembling glass wool. During this change the aldehyde content fell from 96–98 per cent to about 15 per cent without, however, any appreciable increase in free acidity, indicating that the reaction involved was one of condensation rather than of oxidation. Suspecting the influence of traces of alkali derived from the anhydrous sodium sulfate (analytical reagent) used or from the glass bottles, the time of drying was reduced to a minimum and the aldehyde stored in small hard glass tubes at −20° C. during the few days elapsing between purification and use. Under these conditions no further trouble was experienced.

Hydroxylamine Methods. For estimation of the purified aldehyde, modifications of the methods of Bennett and Salamon (*2*) and of Leone and Tafuri (*12*), both employing hydroxylamine, were used. The reagent for the former is prepared by dissolving 5 grams of hydroxylamine hydrochloride in 9 cc. of hot water, adding 80 cc. of 90 per cent alcohol and 0.2 cc. of 0.4 per cent bromophenol blue,[1] neutralizing with alcoholic potassium hydroxide to a greenish blue color, and making up to 100 cc. with 90 per cent alcohol. The aldehyde (1 gram) is added to 20 cc. of this solution and after standing for 20 minutes the liberated hydrochloric acid is titrated with 0.5 *N* alcoholic potassium hydroxide to a clear blue color, the end point being matched with that of a blank determination to which has been added a quantity of alcohol corresponding approximately to the titration obtained. In this way it is possible to obtain much better reproducibility than by attempting to neutralize the reagent exactly before use as recommended in the original method. The purified aldehyde always reacted neutral to bromophenol blue, so that no correction was necessary on this score.

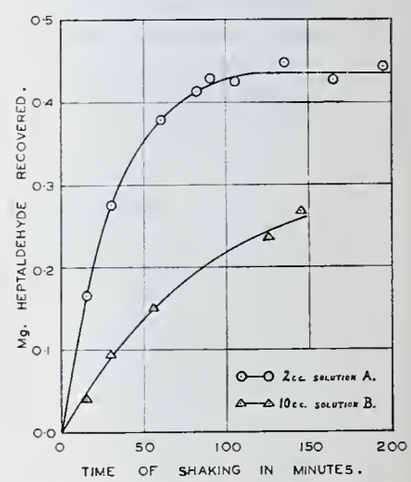

Figure 2. Effect of Volume of Solvent on Rate of Extraction of Heptaldehyde from Benzene

In the Leone and Tafuri (*12*) method the aqueous hydroxylamine solution employed for the determination of acetaldehyde was found to give low results with heptaldehyde and was therefore replaced by a 5 per cent solution of hydroxylamine hydrochloride in 90 per cent alcohol. Twenty cubic centimeters of this reagent are neutralized to phenolphthalein with 1 *N* alcoholic potassium hydroxide, the aldehyde (1 gram) is added, and after standing for 20 minutes the excess hydroxylamine is titrated to

[1] The figure of 2 cc. given in the original paper is presumably a misprint, since it is practically impossible to titrate at this concentration.

methyl orange with standard 0.5 N sulfuric acid. A blank determination is again carried out, water being added in this case to the experiment to compensate for the smaller quantity of acid required. The results obtained were not quite so reproducible and were usually also somewhat lower than those obtained by the Bennett and Salamon method (Table II).

TABLE I. ESTIMATION OF HEPTALDEHYDE BY BISULFITE METHOD

Specimen	Time of Shaking	Normality of Bisulfite Solution 0.1	0.2	0.5	1.0	2.0	5.0
	Min.						
A	30	..	88.8	92.6	94.1	94.1	..
A	60	..	88.2	93.6	93.3	..	94.6
A	90	..	88.5	92.8	93.9	93.7	..
B	60	..	90.4	94.7	96.6	97.0	..
C	30	85.5	91.0	94.9	96.7	96.6	96.3
D	90	84.8	90.3	94.7	96.2	96.2	96.0
E	30	..	..	94.2	95.7	..	..
E	60	..	..	94.5	96.8	..	..
E	90	..	..	94.9	96.6	..	..
F	60	..	..	95.2	96.0	..	..
G[a]	30	..	..	..	79.8	..	..
G	60	75.4	78.0	78.3	79.5	79.6	80.0
H[a]	60	73.7	76.1	79.1	79.4	..	..

[a] Unpurified specimens.

BISULFITE METHOD. In Table I is given a series of results obtained by the bisulfite method. In this case the aldehyde (0.15 gram) was shaken at approximately 240 cycles per minute with 20 cc. of the bisulfite solution in a constant-temperature room at 20° C. The excess bisulfite was then neutralized with iodine, sodium bicarbonate added, and the combined bisulfite titrated with standard 0.1 N iodine. The figures show that no appreciable advantage is to be gained by using concentrations of bisulfite greater than normal, or by shaking for longer than 30 minutes. The values obtained were slightly lower than those given by the hydroxylamine methods.

ESTIMATION OF TRACES OF HEPTALDEHYDE

For the purpose of extracting small amounts of heptaldehyde from a fat the latter was dissolved in a solvent and shaken vigorously with the bisulfite solution in the absence of light. Various solvents were employed in turn, the earlier experiments being carried out with ether, which emulsified readily with the bisulfite, gave more rapid extraction than any other solvent tried, and did not interfere too seriously with the end point of the titration. The blank titration in the absence of added aldehyde or fat was, however, found to increase appreciably with the time of shaking, owing possibly to the production of traces of acetaldehyde, a reaction which is known to occur when ether is allowed to stand in the presence of air, especially in daylight (*6*). In Figure 1 results are given for one of the preliminary experiments in which a solution of heptaldehyde in fresh cottonseed oil (1 gram), ether (5 cc.) and 0.1 N sodium bisulfite solution (25 cc.) were used for each estimation. The lower curve, which has been used to correct the values plotted in the upper, shows the increase in the blank titration (calculated as heptaldehyde) during the experiment. Under the conditions here employed extraction of the aldehyde from the fat is apparently complete in 90 to 100 minutes.

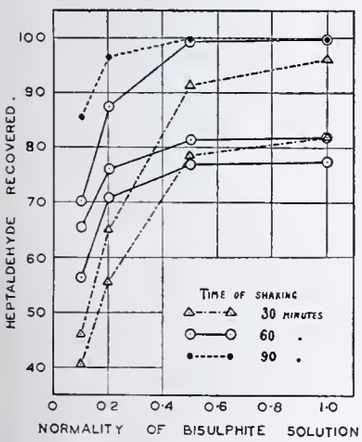

FIGURE 3. EFFECT OF CONCENTRATION OF BISULFITE ON RATE OF EXTRACTION OF HEPTALDEHYDE FROM BENZENE

Two disadvantages are inherent in the above method—namely, the relative instability of the solvent, and the presence of ether and fat in the emulsion to be titrated which makes the end point somewhat difficult to obtain accurately. In later experiments therefore the emulsion obtained after shaking was centrifugalized for 5 minutes and an aliquot portion of the aqueous layer removed for titration. Ether proved unsatisfactory with this technic on account of its volatility and partial miscibility with water, and was replaced by benzene.

The efficiency with which heptaldehyde can be transferred from the benzene to the bisulfite solution will depend upon the volume of benzene employed and the partition coefficient of the aldehyde between benzene and water, as well as the volume and concentration of bisulfite solution and the dissociation constant of the bisulfite compound at the temperature and pH of the reaction. The effect of volume of benzene is shown in Figure 2 in which 2 cc. of solution A of heptaldehyde in benzene or 10 cc. of solution B (one-fifth as strong as A) were shaken with 20 cc. of 0.2 N sodium bisulfite at 20° C. for various lengths of time, centrifugalized, and 15 cc. of the aqueous portion titrated. The results show a much slower and less complete extraction in presence of the larger amount of solvent. In subsequent determinations the volume of benzene was therefore fixed at 2 cc. which is sufficient to hold 1 gram of a solid fat in solution.

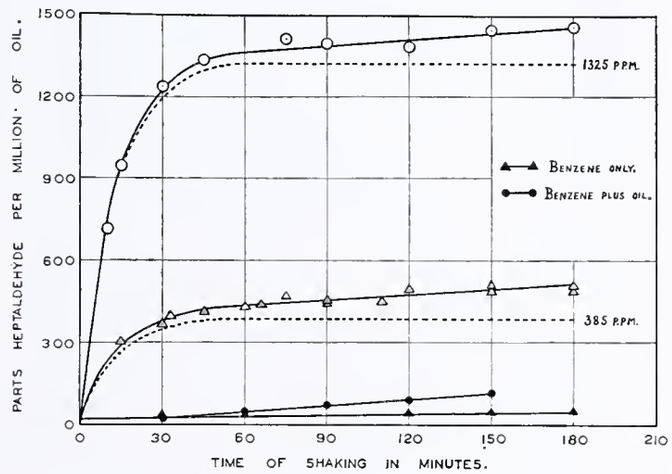

FIGURE 4. ESTIMATION OF HEPTALDEHYDE IN COTTONSEED OIL BY CENTRIFUGE METHOD, USING BENZENE AND 0.5 N SODIUM BISULFITE

The figures given in Table I indicate that the rate of combination of heptaldehyde with sodium bisulfite is influenced to a considerable extent by the concentration of the latter employed. In case of the extraction of small quantities of aldehyde from solution in benzene the effect is still more marked. In Figure 3 are collected the results of a series of experiments in each of which 2 cc. of a solution of heptaldehyde in benzene were shaken with 20 cc. of bisulfite solution of various concentrations for 30, 60, and 90 minutes. Several samples of aldehyde were used, the results being expressed as percentage purity of the sample, those below 85 per cent representing crude commercial samples and those above 95 per cent purified specimens. These results show that with the possible exception of 1 N and stronger bisulfite solutions 30 minutes' shaking is not sufficient to extract the aldehyde completely. Using 60 or 90 minutes, comparatively little advantage is to be gained by increasing the bisulfite concentration beyond 0.5 N. With solutions stronger than normal the estimation becomes difficult owing to fading of the end point when the 0.002 N iodine is being used, and the larger quantities of iodine necessary to destroy the excess bisulfite give rise to so much hydriodic acid and sodium bisulfate as to cause considerable frothing during neutralization with bicarbonate. For subsequent experiments 0.5 N was therefore adopted as the most suitable bisulfite concentration.

Finally a series of determinations was carried out on 2 cc. of a benzene solution of the aldehyde shaken for 30 minutes at 20° C. with 5, 10, 15, 20, and 25 cc. of 0.5 N bisulfite solution, resulting in values of 41.4, 58.0, 70.0, 78.3, and 80.0 per cent

for a sample of crude aldehyde which analyzed to 79.7 per cent by the bisulfite method. The figures indicate that a volume of 25 cc. of bisulfite is desirable; in practice, however, owing to the limited capacity of the centrifuge cups used 20 cc. were found more suitable, the slight loss in efficiency being compensated for by a longer time of shaking.

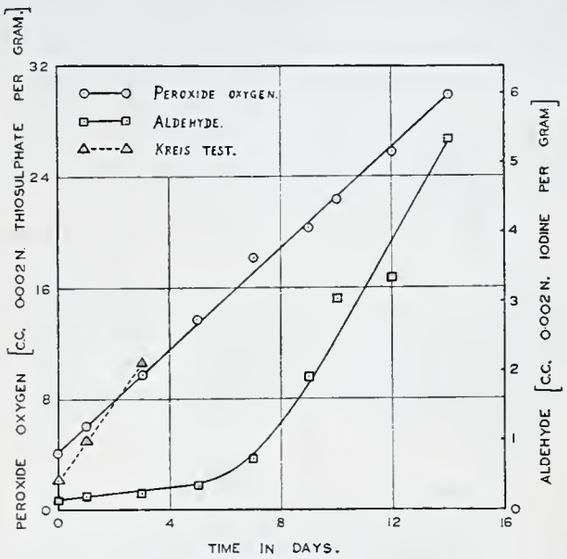

Figure 5. Oxidation of Cottonseed Oil in Lamp Light at 23° to 28° C.

Recommended Method. The bisulfite solution is prepared by dissolving 66.2 grams of anhydrous sodium carbonate in approximately 450 cc. of water, saturating with sulfur dioxide, and making up to 500 cc. with a little sulfur dioxide water. A portion of this stock solution is diluted 10 times when required.

A determination is carried out as follows: Approximately 1 gram of the fat is weighed into each of several glass-stoppered bottles (total capacity about 70 cc.), dissolved in 2 cc. of analytical reagent benzene, warming if necessary, 20 cc. of 0.5 N bisulfite solution are added, and the mixture is shaken at about 240 cycles per minute at 20° C. in the absence of light. At intervals a bottle is removed, the emulsion poured into a tube, centrifugalized at 2000 to 3000 r. p. m. for 5 minutes, and 15 cc. of the clear aqueous layer are pipetted into a 150-cc. Erlenmeyer flask. Iodine is then run in, first 1 N, then 0.05 N, and finally 0.002 N until the excess bisulfite has been destroyed. Should the end point be slightly overrun, a drop or two of dilute thiosulfate may be added, the end point being adjusted to a definite depth of tint, starch and at least 1 gram of potassium iodide of course being present. Sodium bicarbonate (analytical reagent, 3 grams) is now added and standard 0.002 N iodine run in until the same tint is again reached. Towards the end of the titration the color produced by the latest addition of iodine tends to fade more and more slowly, but the true end point is perfectly definite and easy to determine. In this as in the peroxide estimation it has been found preferable to titrate by the aid of a daylight lamp in a darkened room, but this is not, of course, essential.

In Figure 4 are graphed the results of a series of determinations carried out on two solutions of heptaldehyde in fresh cottonseed oil. It can be seen that the blank titration for the benzene alone rises hardly perceptibly (the initial value of about 25 p. p. m. is due to the bicarbonate), but in presence of the oil the increase after 60 minutes becomes rather more marked. When the curves obtained for the aldehyde solutions are corrected for the blank titrations constant values of 1325 and 385 parts per million are obtained, corresponding to 99.2 and 100.3 per cent of the crude aldehyde contents of the two solutions. The specimen of heptaldehyde used analyzed to 98.7 per cent by the Bennett and Salamon method.

In Table II are given analyses of a series of samples of heptaldehyde by the Bennett and Salamon and Leone and Tafuri methods, using in each case approximately 1 gram of material, by the bisulfite method shaking about 0.15 gram of aldehyde with normal or stronger bisulfite for 30 or 60 minutes, and by the same method shaking 1 gram of cottonseed oil or 2 cc. of benzene containing about 0.0004 gram of aldehyde with 0.5 N or 1 N bisulfite for 60 or 90 minutes. The determinations on the dilute solutions actually correspond more closely to the hydroxylamine figures than do the bisulfite estimations on the aldehyde itself.

Table II. Estimation of Heptaldehyde in Dilute Solution by Bisulfite Method

Hydroxylamine Methods		Bisulfite Method		
Bennett and Salamon	Leone and Tafuri	Aldehyde alone	Benzene solution	Cottonseed oil solution
96.3	95.1	94.0	..	..
98.3	96.3	96.3	99.5	..
98.7	97.5	96.5	..	99.2
98.5	97.2	..	99.5	..
97.4	95.9	..	..	97.9
96.4	94.6	..	95.8	..
97.5	96.7	95.6	97.1	..

Aldehyde Determinations on Oxidized Fats

Aldehyde determinations have as yet been carried out on relatively few natural fats, but preliminary experiments indicate that zero values are obtained from perfectly fresh samples. The method employed in all cases has been that described above, the time of shaking being 60 minutes and appropriate correction being made for the blank titration on the reagents. [Mean values for the blank titration (15 cc.) in the absence of fat were 0.17, 0.20, 0.24, and 0.27 cc. of 0.002 N iodine for 30, 60, 90, and 120 minutes' shaking.] With continued shaking perceptibly higher results are obtained (Table III), but the shorter period has been adhered to in order to minimize any danger of aldehyde production during the determination.

In Figure 5 data are given for the oxidation of a specimen of cottonseed oil illuminated at 22° C. by a 100-watt lamp at a distance of 3 feet (90 cm.), 20 cc. of the oil being placed in each of a series of flat-bottomed glass dishes 6 cm. in diameter, one of which was removed at intervals for examination. The Kreis test was carried out by dissolving the oil (3 grams) in benzene (6 cc.) in a glass-stoppered cylinder, and shaking with concentrated hydrochloric acid (3 cc.) for 1 minute. Five drops (0.1 cc.) of a 5 per cent solution of phloroglucinol in alcohol were then added, the mixture reshaken for 1 minute and separated by means of the centrifuge. Approximately 2 cc. of the clear aqueous layer were transferred to a 1-cm. glass cell and matched against the color standards of the Lovibond tintometer (B. D. H. pattern, with artificial light attachment). By use of a little yellow or blue (depending on the nature of the fat) in conjunction with the red an accurate match can readily be obtained. The values plotted in Figures 5, 6, and 7 on the same scale as the peroxide oxygen figures are the sums of the red and yellow or red and blue glasses required. In case of samples of fat giving colors

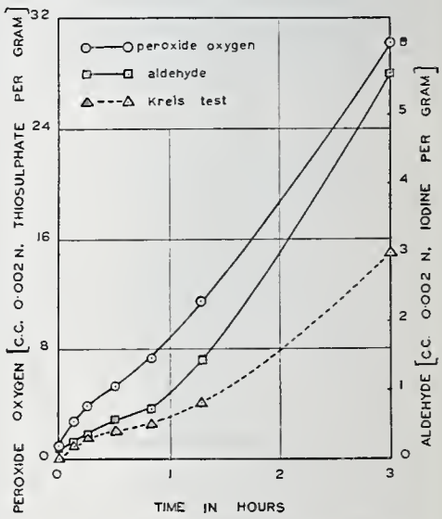

Figure 6. Oxidation of Butter Fat in Direct Sunlight

deeper than about 10 units on the Lovibond scale the amount of fat used must be reduced and the observed value corrected back to the normal weight.

Figure 6 gives the results of an experiment in which butter fat (20 cc.) was exposed in Petri dishes (15 cm. diameter) to direct sunlight for 3 hours. All the specimens of fresh butter fat examined gave Kreis tests of O.OR, 0.5Y; which figure has therefore been treated as a blank and subtracted from the subsequent readings.

A second sample of butter fat oxidized under conditions similar to those employed for the cottonseed oil gave the results expressed in Figure 7. In this latter experiment the Schibstead test was carried out exactly as described by the author, the solutions being matched in a Duboscq colorimeter. It is, however, somewhat simpler to calibrate the cresol red standard against the Lovibond color glasses (4.75R, 1.1B in 1-cm. cell), after which the experimental solutions can be matched directly in the tintometer. The color of light transmitted through 1 cm. of the melted butter fat is expressed in Lovibond units and plotted on the same scale as the peroxide oxygen and Kreis values.

Table III. Effect of Time of Shaking on Apparent Aldehyde Content of Oxidized Fats

Fat	Time of Shaking 30 min.	60 min.	90 min.	120 min.
Fresh beef fat[a]	0.0	0.0	0.0	0.0
Fresh butter fat[a]	0.0	0.0	0.0	0.0
Oxidizing butter fat	0.0	0.1	0.1	0.1
Oxidizing butter fat	0.2	0.2	0.2	0.2
Oxidizing butter fat	0.4	0.5	0.6	0.5
Oxidizing butter fat	0.4	0.7	0.7	0.7
Oxidizing butter fat	0.6	0.8	0.8	0.8
Oxidizing butter fat	0.8	1.0	1.2	1.2
Oxidizing butter fat	1.2	1.6	1.6	1.7
Oxidizing butter fat	8.4	10.5	10.6	10.8
Fresh lard[a]	0.0	0.1	0.1	0.1
Oxidizing lard	0.8	1.2	1.6	1.7
Oxidizing lard	1.0	1.5	1.7	1.9
Fresh cottonseed oil[b]	0.0	0.1	0.4	0.4
Oxidizing cottonseed oil	0.1	0.3	0.4	0.4
Oxidizing cottonseed oil	0.3	0.7	0.7	1.0
Oxidizing cottonseed oil	1.6	1.9	2.0	2.3
Oxidizing cottonseed oil	2.3	3.0	3.2	3.3
Oxidizing cottonseed oil	2.8	3.3	3.5	3.5
Oxidizing cottonseed oil	4.8	5.3	5.6	5.6

[a] Laboratory extracted.
[b] Commercial.

Table IV. Standardization of Thiosulfate Solutions

Method	Without Carbonate 0.002 N	With Carbonate 0.002 N	0.1 N
Bichromate (acid)	97.2	97.2	99.6
Iodate (acid)	99.8	99.8	100.0
Iodine (acid)	100.0	100.0	100.0
Iodine (no acid)	100.4	104.2	100.4
Iodine (bicarbonate)	102.9	...	...

The pronounced lag in the appearance of aldehyde in cottonseed oil (Figure 5) as compared with the butter fat in Figures 6 and 7 is of interest in view of the ability of the former to absorb much larger quantities of oxygen at ordinary temperatures without developing perceptible rancidity. The similarity in shape of the peroxide-oxygen, fat aldehyde value, aldehyde content, Kreis test, and bleaching curves shown in Figure 7 is also rather striking. Further work utilizing the aldehyde estimation method is in progress.

Discussion

Dilute thiosulfate solutions are often standardized against 0.01 N bichromate prepared by weighing out the exact amount of the dry analytical reagent salt. This method possesses the advantage that the bichromate solution is quite stable, and when precautions are taken in running a blank on the reagents and titrating in the absence of daylight perfectly consistent results can be obtained. It has been found, however, that the values given by the bichromate method are distinctly in error. Further, as can be seen from Table III, the common practice of adding a trace of sodium carbonate (0.1 gram in 5 liters) to thiosulfate solutions for the purpose of preventing precipitation of sulfur can lead to serious inaccuracy with dilute solutions unless the titration against iodine is carried out in presence of acid. It is probably preferable, therefore, whether carbonate has been added or not, to standardize dilute thiosulfate solutions against iodine in the presence of a little acid, the results obtained in this manner agreeing closely with those of the iodate method.

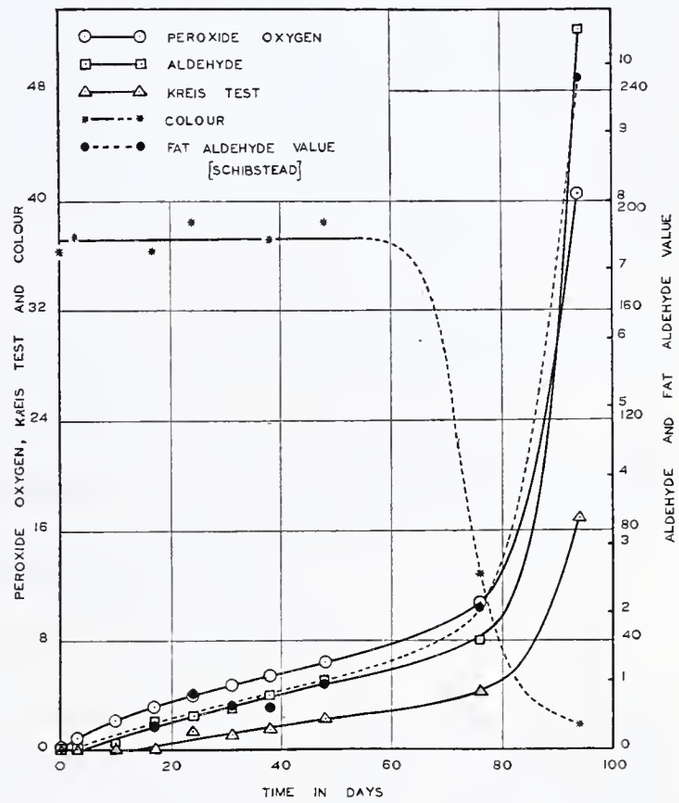

Figure 7. Oxidation of Butter Fat in Lamp Light

Bisulfite Titration. In the determination of small quantities of aldehydes by the Clausen method the combined bisulfite is liberated by addition of sodium bicarbonate and titrated with iodine in the presence of the excess of bicarbonate. If, however, a blank determination is carried out without the aldehyde, and, after addition of the bicarbonate, a known amount of sodium bisulfite is run in and titrated with iodine, an incorrect result is obtained. For example, 25 cc. of a bisulfite solution actually equivalent to 25.7 cc. of 0.002 N iodine (standardized by running the bisulfite from the buret into the acidified iodine solution) neutralized only 12.3 cc. of iodine under the conditions of the determination, though by omission of the bicarbonate the figure could be raised to 25.1 cc. By running in the bisulfite approximately 1 cc. at a time and immediately neutralizing with iodine a titration of 25.1 cc. was, however, again obtained even in presence of the bicarbonate. This latter observation probably accounts for the fact that no large error arises in the actual estimation of aldehyde, most of the bisulfite being oxidized as soon as it is liberated.

Two modifications of the standard method were investigated. In the first the bicarbonate was added slowly as a 10 per cent solution. The first 8 or 10 cc. being used in neutralizing the acid present produced practically no liberation of bisulfite, which was however almost completely liberated by the next 1 or 2 cc., the remainder of the bicarbonate being added only at the end of the titration to insure complete reaction. The results obtained were identical with those of determinations in which the solid bicarbonate had been used.

In the second modification, after neutralization of the excess bisulfite a quantity of standard iodine equal to approxi-

mately twice that which would be required to oxidize the combined bisulfite was added, followed by the bicarbonate in the usual way, the excess iodine being titrated with thiosulfate solution. A blank determination without the aldehyde sufficed to standardize the thiosulfate. Several determinations carried out by this method on a sample of heptaldehyde (0.15 gram) gave consistent results rather higher than those obtained by the usual technic, and, since they agreed closely with the Bennett and Salamon method, probably more correct. Dilute bisulfite solutions (0.002 N) could also be estimated satisfactorily in this way, but applied to solutions of heptaldehyde in cottonseed oil erratic results were obtained, the blank determination on the fresh oil being high and irregular. The back-titration method was therefore abandoned in favor of the ordinary technic described above, which as can be seen from Table II gives consistent and sufficiently accurate results.

Acknowledgment

The author wishes to express his thanks to L. J. Parr for assistance with the experimental work.

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Heat-of-Solution Method in the Calorimetry of Portland Cement

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The study of the thermochemistry of cement has recently been given considerable impetus by such practical application as the specification of heat evolution limits during hardening for cement used in construction of the Boulder Dam. Fundamental to such studies is an accurate calorimetric method and this article indicates the precautions necessary to attain a reasonable accuracy. The method given is especially designed for measuring the heat of hydration of cement at various ages.

Zinc oxide is suggested as a suitable secondary standard for heat capacity determinations.

The measurement of the heat evolution of Portland cement during hardening has been the subject of numerous investigations during the past two years (*2, 6*), and has reached the stage of practical application in mass concrete construction. Thus the cement used in the construction of the Pine Canyon Dam[1] (City of Pasadena, Calif.) and of the Boulder Dam has been subject to restrictions of heat development at 7 and 28 days (*3,4*).

The heat-of-solution method as proposed by Woods, Steinour, and Starke is probably the most accurate of those used thus far, and although it may be replaced by less expensive methods for routine work, it will undoubtedly continue in use for research and referee tests. For this reason it was thought desirable to make available the results obtained by the authors during the investigations of the heat evolution characteristics of cement furnished for construction of the Pine Canyon Dam, and to point out the sources of error in the method and means of avoiding them. The principle of the method is scientifically sound and requires simply the measurement of the heat of solution of the dry cement and of the hydrated cement in a suitable acid charge, the difference between the two values obtained being the heat of hydration.

The apparatus is shown diagrammatically in Figure 1, being modeled after that of Woods et al. (*6*), and follows the principles of calorimeter design given by White (*5*). It consists essentially of a gold-lined reaction vessel into which the cement to be tested is introduced. The temperature rise is measured by a copper resistance thermometer, and the heat capacity is determined by means of a manganin wire heater coil and a potentiometer. A platinum stirrer is used to maintain a uniform distribution of temperature. The calorimeter is immersed in a water bath which is closely regulated at 30° C. The cement sample is contained in a stoppered glass tube which has a rod and ground-glass valve to permit the introduction of the sample into the acid. The acid charge consists of 1200 grams of nitric acid (normality 2.000 ± 0.002) and 22.5 grams of 48 per cent hydrofluoric acid. Six grams of dry cement and a weight of the hydrated cement which gives approximately the same temperature rise constitute the cement charge.

[1] This structure has recently been renamed the "Morris Dam."

Procedure

The procedure may suitably be divided into four distinct operations: preparation of the sample for hydration; weighing of the calorimeter sample; operation of the calorimeter; and calculation of results. The principal features of these operations will be discussed here; the detailed procedures must be adapted to the particular apparatus used.

Preparation of the Sample for Hydration. The dry cement is mixed with pure water to give a water-cement ratio of 0.40 and is stored for one day at 70° F. (21.1° C.), then at 100° F. (37.8° C.) until the time of test, which is at 7 days' and at 28 days' total elapsed time. This time-temperature curve is of course entirely arbitrary, but lends itself well for laboratory testing and does not differ greatly from that actually found to exist in mass concrete construction. It is

obvious that any curve whatever would be just as arbitrary since the temperatures in the structure itself are not uniform. The effect of different curing temperatures upon the heat of hydration is shown in Figure 6 and will be discussed below.

The water-cement ratio of 0.40 corresponds to that used in mortar compression test specimens but differs from that actually used in the concrete of the dam, which is nearer 0.6. However, the heat development with different ratios may be determined by suitable auxiliary tests, such as are shown in Figure 5.

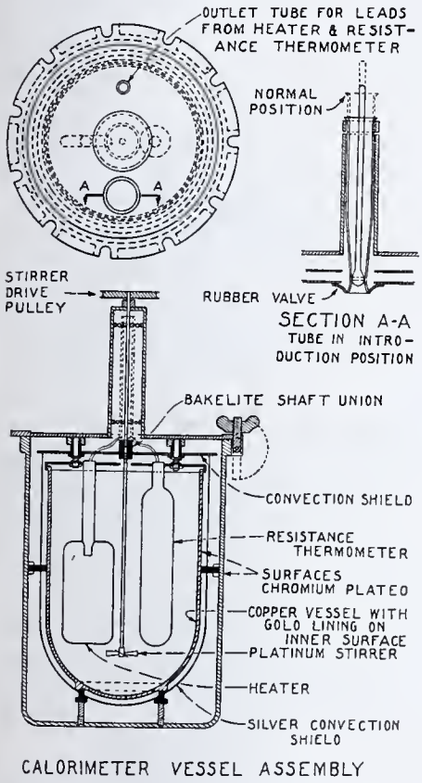

Figure 1. Diagram of Apparatus

The principal precaution to be observed in preparing the sample is that each container (4-dram homeopathic vials were used) shall contain a truly representative portion of the water-cement mixture. Since there is some tendency for the cement to settle, it is not advisable to pour the mixture from a cup unless thorough stirring is continued during the process. A convenient arrangement is that shown in Figure 2. The manually operated screen stirrer does not beat air into the mixture, as is usually the case with the ordinary propeller type. The stirring is continued while the cork is withdrawn and the vials filled. The reproducibility of different vials from the same pour as shown in Table II indicates that the desired result has been accomplished. It is essential that the hydrated cement be sealed in its containers during storage, so that no water will escape or air be introduced.

Weighing Procedure. The dry cement is safely handled in the air when exposure is not longer than that required to weigh the sample by the usual methods.

Two sources of error in preparing the hydrated sample for the calorimeter must be carefully guarded against if reproducible results are to be obtained. The sample will of course have "set" in its container during the hydration period, so that it must be ground before weighing. During the grinding and weighing processes it is exposed to the laboratory atmosphere, and it has been found that undue exposure of this kind causes it to absorb carbon dioxide from the air, resulting in a lowered heat of solution. The magnitude of the effect is shown in Table I and indicates that the exposure must be kept to a minimum, especially when the sample is still quite moist—i. e., at the earlier ages. The most effective means of accomplishing this purpose is to grind the sample as rapidly and as coarsely as the procedure will permit (a 10-mesh sieve size has been found satisfactory). The advantage of using a 10-mesh sieve size instead of the 100-mesh which has usually been specified can be readily seen in that the grinding time is reduced to one-third and the surface area probably to $^1/_{100}$ of the values for the finer grinding. This is clearly indicated in Table II, which shows the results obtained on four different vials from the same pour, each sample being ground first through the 10-mesh and then through the 100-mesh sieve. As has been stated, the effect of exposure is greater at the earlier ages, which is reflected in the 7-day group. The average difference of 1 calorie between the two sets at 7 days has been found consistently in other tests. Thus the magnitude as well as the reproducibility of the results is affected by the change in procedure, and shows the care required to obtain reliable results.

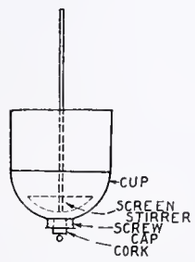

Figure 2. Mixing Apparatus

Table I. Effect of Exposure of Hydrated Cement to Various Atmospheres

(Sample: Riverside 19R4)

Treatment	Heat of Solution 7 days 10 mesh	7 days 100 mesh	28 days 10 mesh	28 days 100 mesh
	Cal./g.	*Cal./g.*	*Cal./g.*	*Cal./g.*
Normal	535.6	534.7	526.4	525.4
Exposed to air 4 hrs.	525.9	521.7	518.1	510.3
Exposed in desiccator 4 hrs.	535.2	534.2	527.3	525.9
Exposed to saturated CO_2 for 10 min.	502.3	484.0	497.9	477.3

Table II. Reproducibility of Heat of Solution of Hydrated Cement Ground to Pass 10-Mesh and 100-Mesh Sieves

Vial	Heat of Solution 7 days 10 mesh	7 days 100 mesh	Vial	Heat of Solution 28 days 10 mesh	28 days 100 mesh
	Cal./g.	*Cal./g.*		*Cal./g.*	*Cal./g.*
1	532.9	532.3	2	519.0	520.2
3	533.3	531.2	4	520.9	520.1
5	533.7	533.3	6	519.6	520.1
7	533.5	531.5	8	519.8	519.9
Av.	533.3	532.1	Av.	519.8	520.1

The other source of error is associated with the weighing procedure, because of the fact that the sample is quite moist and loses water rapidly upon exposure to the atmosphere. The usual procedure of differential weighing of the calorimeter sample and the ignition sample successively from the same weighing bottle is subject to considerable error when the sample is moist. This error may be made negligible by use of a suitable technic—e. g., the sum of the calorimeter sample and that for ignition may be roughly weighed into a bottle, then thoroughly rolled in the bottle, and the ignition sample quickly removed in one operation.

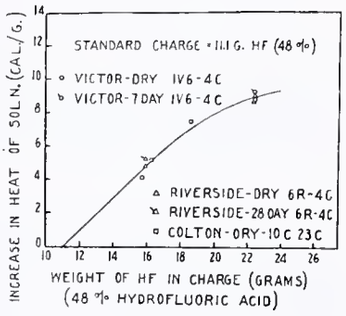

Figure 3. Effect of Hydrofluroic Acid Concentration on Heat of Solution

If these precautions are observed, the error in the heat of solution of the hydrated sample will be no greater than that in the dry sample.

Calorimeter Procedure. The quality of the results of the calorimeter tests depends primarily upon the accuracy of the temperature measurements and heat capacity determinations. The resistance thermometer is carefully calibrated against a Bureau of Standards Beckmann thermometer and suitable calibration charts are made. The heat capacity is determined by introducing a measured quantity of electrical energy and noting the resultant temperature rise. The operating technic will of course be peculiar to each apparatus and need not be given here.

Calculation of Results. A discussion of the calculation of the heat of hydration of the cement from the calorimetric data has been given in the literature (*1*). The required pre-

cision makes it necessary to take into account fully all the sources of error which are encountered and to make adequate corrections therefor.

Effect of Hydrofluoric Acid Concentration

The heat of solution of cement is rather sensitive to the concentration of hydrofluoric acid in the charge, so that suitable corrections must be made if the concentration differs materially from the standard. Figure 3 shows the variation of the heat of solution with the amount of hydrofluoric acid used and may be used as a basis for these corrections. The specifications originally prescribed a hydrofluoric acid concentration of 10 ml. of 48 per cent acid per charge, but were later modified to double this quantity because some of the cements showed incomplete solution with the smaller amount of the acid present.

Differential Heat-of-Solution Effect

A correction to the heat of solution must be made when a weight of cement is used in the charge which differs from the standard weight which has been decided upon (6 grams in this case). This arises from the fact that successive increments of cement added to the acid do not give the same heat of solution per gram, and is called the differential heat-of-solution effect. Its magnitude is determined empirically from data such as those plotted in Figure 4. It is evident that this effect is only one-third as great when 20 ml. of hydrofluoric acid are used in the charge than when 10 ml. are used, and is an advantage of the use of the greater quantity, in addition to the more rapid and complete solution which is obtained.

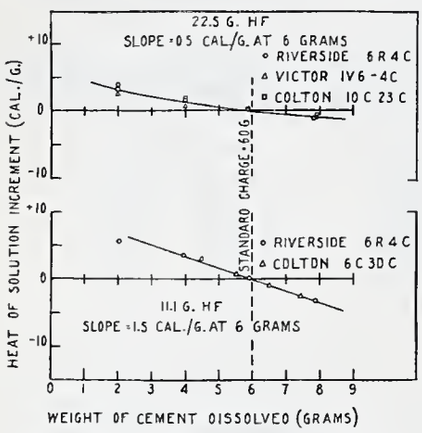

Figure 4. Differential Heat-of-Solution Effect

Heat of solution at 6.0 grams taken as reference point.

Temperature Coefficient of Heat of Solution

The heat of solution of cement also varies with the temperature at which the tests are made. Table III shows the results of experiments made to determine the temperature coefficient of the reaction, which turns out to be about − 0.3 calorie per gram per ° C. in the range from 15° to 30° C. This coefficient will of course apply only to the low-heat cement for which it was determined, but probably does not vary greatly with the chemical compositions ordinarily encountered.

Table III. Temperature Coefficient of Heat of Solution of Cement

Sample	Heat of Solution 17.1° C.	Heat of Solution 29.9° C.	Difference
	Cal./g.	*Cal./g.*	
Victor 1V6-4c	590.0	585.7	4.3
Riverside 6R4	590.4	586.2	4.2

Temperature coefficient = −0.33 cal. per ° C.

Effect of Change in Water-Cement Ratio

Since the water-cement ratio actually used in the concrete of the dam differs from that used in the test specimens, it is important to know what effect upon the heat development is brought about by a change in this ratio. The results of tests on two different cements are shown by the curves in Figure 5. The water-cement ratio was varied from 0.40 (used in the tests) to 1.0. The ratio used in the concrete of the dam was about 0.6 and is indicated by the broken line. Instead of the smooth curves which might be expected, consistently angular graphs are obtained.

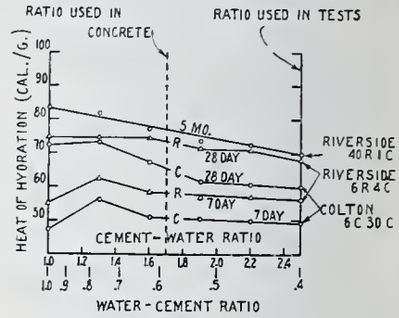

Figure 5. Effect of Water-Cement Ratio upon Heat of Hydration

The irregularities may be due to the fact that it was difficult to maintain the cement in uniform suspension during the curing period. The vials in which the cement was placed were rotated horizontally for 2 days to prevent segregation, but in the case of the higher water contents a portion of the mix acquired a set after about 24 hours, leaving some free water at one end of the vials. In those having the lower water-cement ratios the mixture appeared to set without noticeable segregation. It is probable that in the less homogeneous mixtures the conditions of hydration are not uniform and therefore not comparable with those in which no segregation takes place.

In order to calculate the heat evolved by the cement under the conditions in which it was used in the concrete of the dam, it appears necessary to add a definite fraction to the values obtained in the tests. These are 2.5 per cent at 7 days, 5 per cent at 28 days, and about 10 per cent at 5 months.

It is difficult to explain the nature of these curves in any simple manner; there are evidently a number of complicating factors, such as the hydrolysis of the cement compounds, etc., whose effects cannot be separated by means of the data obtained.

Effect of Change in Curing Temperature

Since the particular time-temperature curve used in curing the test specimens will be different from that to which the concrete in the dam is subjected, it is of interest to know what the general effect is of a change in curing temperature conditions. Figure 6 shows the results obtained with a Riverside low-heat sample for curing temperatures of 70°, 100°, and 212° F. (21.1°, 37.8°, and 100° C.) continuously, as well as the standard of 70° F. for 1 day and 100° F. thereafter. It is significant that while the rates of heat development differ markedly for the different temperatures, yet the ultimate value seems to be nearly the same. This would indicate that the temperature coefficient of the reaction is rather small. It should also be noted that the ultimate value is reached

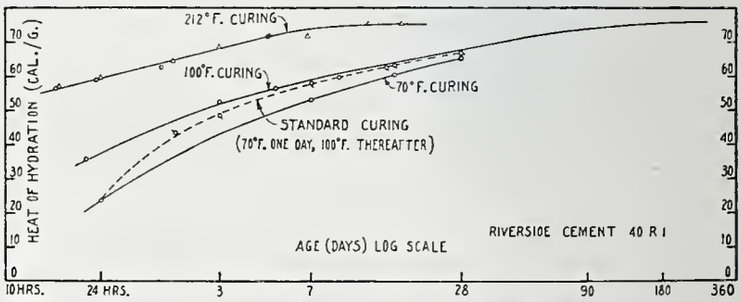

Figure 6. Effect of Curing Temperature upon Heat of Hydration

in less than 14 days by the sample cured at 212° F., whereas those cured at 70° and 100° F. require 6 months or more to reach a maximum. It is clear that when it is desirable to know the ultimate heat developed by the cement, a curing temperature of 212° F. would be advantageous in greatly accelerating the reaction. The results here shown are of course to be considered as preliminary and merely indicative of the possibility of using elevated temperatures for accelerated tests. It is likely that valuable information on the thermochemistry of the cement reactions may be obtained by further studies along these lines.

Zinc Oxide as a Secondary Standard in Heat Capacity Determinations

The electrical calibration of the calorimeter to determine its heat capacity is probably the most reliable method of obtaining an accurate absolute value. However, it is somewhat tedious and gives a temperature-time curve which is unlike that obtained with cement. There is also the possibility that the heater may be attacked by the acid and rendered useless for calibration purposes. Therefore it was desirable to find a chemical substance which might be used as a secondary standard. Calcium oxide has been proposed, but its high reactivity with moisture and carbon dioxide introduces manipulation difficulties, in addition to the precipitation of calcium fluoride which it produces in the acid charge. After some investigation it was found that zinc oxide was suitable for the purpose, being only slightly hygroscopic and giving a highly reproducible heat of solution. The best results are obtained if the zinc oxide is first ignited at about 950° C. for several hours. It goes into solution very rapidly and produces a time-temperature curve which approximates that of a cement, in contrast to the electrical heating which gives a slow temperature rise.

Table IV shows a series of results obtained with the substance and indicates its suitability as a standard of this kind. In one set of comparative tests it was found that both Merck C. P. and Baker C. P. samples gave the same value.

Table IV. Reproducibility of Calorimeter Tests

Heat Capacity of Calorimeter		Heat of Solution				
		Dry cement 6C30		Zinc oxide (C. P., ignited)		
Date	*Cal./° C.*	*Date*	*Cal./g.*	*Date*	*Cal./g.*	
Apr. 17	1165.3	Dec. 20	572.8	May 10	256.65	Lot 1
May 3	1163.5	Dec. 30	572.5	May 10	256.69	Lot 1
May 19	1162.6	Dec. 31	573.0	May 10	256.70	Lot 1
June 26	1163.3	Feb. 1	573.8	June 27	256.56	Lot 2
July 26	1164.8	Feb. 7	572.6	July 26	256.75	Lot 2
Sept. 20	1164.1	Feb. 17	573.1	Sept. 20	256.55	Lot 2
Dec. 14	1162.5			Dec. 5	256.10	Lot 3
		Av.	573.0	Dec. 5	256.00	Lot 3
				Dec. 14	256.34	Lot 3
Av.	1163.7			Av.	256.48[a]	

[a] Using heat capacity 1163.7, average heat of solution is 256.1.

Reproducibility of Results

It was found that by exercise of the precautions given above, the errors could be reduced to those which may be called purely calorimetric—i. e., involving errors due to the calorimeter alone. Tables II and IV show the kind of reproducibility of which the calorimeter is capable and indicate that the probable error in the heat of solution tests is less than one calorie. Such accuracy is quite satisfactory when the number of operations involved is considered, but its price is great care and skill in conducting the operations.

Acknowledgment

The authors are indebted to R. G. Folsom, R. A. Brown, and J. L. Dickinson for their suggestions and skillful work which have made possible whatever advance in cement calorimetry has been made during these investigations.

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Dilution Method for Micro-Kjeldahl Determinations

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The use of sulfuric acid as a dilution medium in micro-Kjeldahl determinations, where no microbalance is available, is convenient for materials insoluble in water, such as wool and silk, and reduces the time of digestion as compared with that required for water solutions. So far as the writer is aware, this has not been previously suggested in the literature.

Rapid solution occurs, without charring, when wool is heated with concentrated sulfuric acid in a thick-bottomed container, over a hot plate, with frequent shaking to avoid local overheating. A 0.2-gram wool sample will dissolve in 10 cc. of sulfuric acid in 3 to 5 minutes, giving a clear amber solution. Since special volumetric flasks with thick bottoms would be needed to apply a volumetric method, the solution was carried out in this laboratory in 30 cc. dropping bottles. Portions containing 25 drops were then transferred to micro-Kjeldahl digestion flasks, the weights determined by difference, and the catalyst added.

The amount of catalyst may also be regulated by dissolving it in sulfuric acid and using a definite number of drops. Selenium, which was found to give much quicker results with wool than Pregl's $CuSO_4$–K_2SO_4 catalyst, was prepared in 1 per cent solution by strongly heating reduced selenium in concentrated sulfuric acid, until it dissolved to a pale yellow solution. A round-bottomed flask is required. A 1 to 1 ratio of selenium to wool is the optimum concentration. The digestion liquor is clear within 15 minutes, but 25 to 30 minutes should be allowed for complete nitrogen recovery. Hydrogen peroxide is seldom required.

It was also found advantageous to use a volume rule instead of Pregl's[1] time rule for the steam distillation in Parnas and Wagner's micro-Kjeldahl apparatus. Distillation is continued until 10 cc. of distillate have condensed in the receiver. Graduated centrifuge tubes of 50 cc. capacity are satisfactory for collection and subsequent titration and boiling.

Aliquots of the same wool solution checked within 1 part in 160. Typical results were 16.23, 16.11, and 16.18 per cent of nitrogen in a wool blanket composed of two parts of three-eighths blood and one part of one-quarter blood wool, and 16.00, 16.01, and 15.93 per cent of nitrogen in a wool blanket containing one part of one-quarter blood wool and two parts of reworked wool.

Received March 24, 1934.

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Modified Hydrogen Evolution Method for Metallic Magnesium, Aluminum, and Zinc

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Chemically this method is the same as the Meyer hydrogen evolution method (*2*), depending on the measurement of hydrogen gas evolved by metals acting on dilute sulfuric acid. The apparatus and technic used, however, offer a quicker, more convenient, and more accurate way of determining metallic magnesium, aluminum, and zinc than is obtained by the Meyer method.

The glass immersion filter (*3*), which is the essential feature of this method, affords a means of controlling the speed of reaction by allowing acid to be drawn into or driven out of the reaction tube at will by the simple expedient of lowering or raising the leveling bulb. In the same way any accumulation of salts formed by the reaction can be flushed out at regular intervals without danger of losing gas, keeping the surface of the metal constantly exposed to fresh acid. When the evolution of gas is completed, it can easily be drawn into the eudiometer without any difficulty from trapped gas bubbles, which one frequently encounters in the regular method.

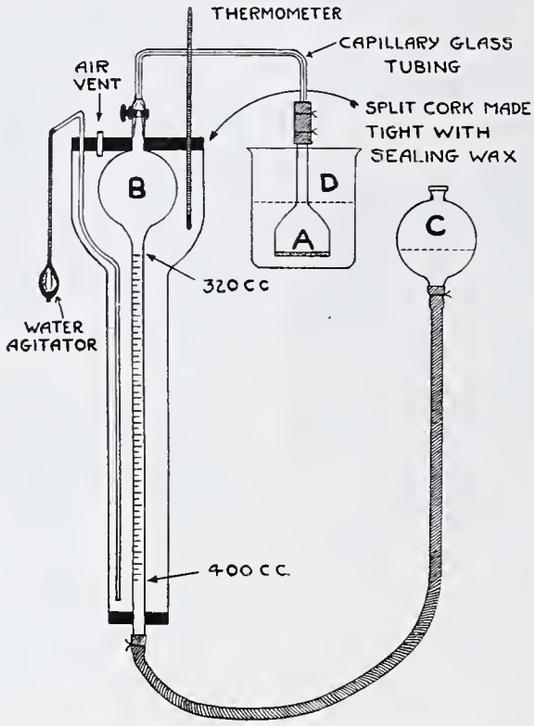

Figure 1. Diagram of Apparatus

The immersion filter used was made of Jena glass, with a fused-in sintered filter disk 3 mm. thick. These tubes are made in three degrees of porosity—coarse, medium, and fine. The tube used was of medium porosity, and was of 30 cc. capacity. The other parts of the assembled apparatus are illustrated in Figure 1.

The eudiometer tube was especially designed for this method. As illustrated it has a capillary tube on top for entrance of gas, and is graduated in 0.1 cc. between the 320-cc. and 400-cc. mark.

Procedure

The apparatus is assembled preferably in a room with fairly even temperature and no drafts.

All rubber connections are made secure with wire, and eudiometer tube *B* is filled completely with distilled water, saturated with hydrogen. The metal, equivalent to about 360 cc. of hydrogen gas at standard conditions of temperature and pressure, is weighed into the dry immersion filter, *A*. (The eudiometer was calibrated from 320 to 400 cc.) A piece of thick-walled rubber tubing, of 0.188 inch (0.47 cm.) inner diameter and 4 inches (10 cm.) in length, is next connected with the filter. Distilled water saturated with hydrogen is poured rapidly into the filter until it flows over the top of the tubing, at which time a pinchcock is clamped on the rubber tubing, stopping the flow of water through the porous filter and preventing air from entering the tube from the top.

While filling, the slow downward flow of water through the porous disk keeps the finer mesh metals in the bottom of the tube. By using hydrogen-saturated water, preferably at 15° to 20° C., in filling the tube little difficulty is experienced even with very fine magnesium powder of a high degree of purity. A spring-type pinchcock, which can be operated with one hand, is the best to use, leaving the other hand free for pouring. After clamping the pinchcock and making sure the rubber tubing is completely filled with water, the reaction bulb is connected to the eudiometer as shown. About 1 inch (2.5 cm.) of distilled water is poured into beaker *D* around the reaction tube, and the pinchcock is removed.

The reaction can now be started A little concentrated sulfuric acid is poured into beaker *D*, the stopcock on the eudiometer opened, and leveling bulb *C* slightly lowered, so as to draw a little acid into the immersion filter. At first, caution should be used so that the flow of gas is slow, until a gap is formed between the levels of liquid in *B* and *A*. Action is then increased by lowering *C* as required. About two or three times during a determination leveling bulb *C* is raised, and the liquid in *A* partially expelled. On lowering *C* again, fresh acid is drawn in and the reaction continues with renewed vigor. On completion of reaction, leveling bulb *C* is slowly lowered and all remaining gas in *A* and in the tubing is drawn into the eudiometer and after standing 5 minutes is measured in the usual way.

Barometer and temperature readings are closely checked and calculation made according to the formula

$$\frac{PV}{T} = \frac{(P' - v)V'}{T'} \times \frac{1 - (0.00018 \times t)}{1}$$

$\frac{V}{X} \times 100$ = per cent free metal in sample

X = volume of hydrogen, under standard conditions of temperature and pressure, generated by same weight of metal of 100 per cent purity

This method has been used successfully with magnesium samples of various degrees of purity and fineness, and has been found applicable for all grades up to and including 150-mesh material.

Table I. Results of Laboratory Tests

Metal	Modified Gas Evolution Method	Copper Oxide Method(*1*)	Aluminum Chloride Method(*1*)
Magnesium ribbon	99.89	...	...
	99.88	99.87	...
Magnesium 35–80 mesh	98.11	98.30	...
	98.11	98.28	...
	98.16	98.41	...
	...	98.15	...
Magnesium 100-mesh	97.51	97.47	...
	97.68	97.64	...
	...	97.35	...
Magnesium 100-mesh. Sample 120	99.09	98.99	...
	99.20	99.21	...
	...	99.09	...
Magnesium 150-mesh. Sample A	92.40	...	...
	92.41	...	...
	92.33	...	...
Magnesium powder. Sample D. 100-mesh	97.42	97.81	...
	97.67	97.71	...
	97.88	97.50	...
Magnesium powder 5	95.13	95.18	...
	94.85	...	...
Aluminum wire	99.70	...	99.81
	99.73	...	...

Zinc and aluminum (but not aluminum powder) can also be determined in this way. In the case of aluminum, a sodium hydroxide solution is used as a reagent.

Some results obtained at this laboratory by different analysts over a period of about 4 years are given in Table I.

The time required for an analysis of magnesium varied from 2 to 4 hours, depending on the temperature of the room. No heat was applied to speed up the reaction, but could doubtless be used to advantage when the room temperature is very low or when less reactive metals than magnesium are being analyzed.

Acknowledgment

The author wishes to thank J. A. O'Callaghan, T. C. Jenkin, and F. Thames of this laboratory for analytical work done in connection with this method.

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Furoic Acid as an Acidimetric Standard

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The suitability of furoic acid as a primary standard was suggested by experience gained in purifying the acid for use of its derivatives as bactericides. In these experiments it was necessary to prepare by sublimation from the technical grade an acid of the highest purity. The acid was then titrated with an alkali previously standardized by the Bureau of Standards—Standard Samples No. 39d, benzoic acid, and No. 84, acid potassium phthalate. It was observed that the purified furoic acid could be titrated with the standardized alkali to a high degree of accuracy and that this titration afforded the most rapid and accurate method of determining the purity of the sample of furoic acid, which finally led to the determination of its applicability as a standard.

The method used in studying the applicability of furoic acid was indirect, standardizing the standard alkali by Bureau of Standards samples.

Upon analysis the furoic acid showed the following results:

Melting point	128–9° C.
Moisture	0.25%
Nonvolatile matter	0.02%
Acidity (as furoic acid with phenolphthalein)	99.72%

This sample was purified by crystallization from water. After drying, the melting point was found to be 129.6° C. After subliming the melting point became 131° C.; resubliming gave no change in the melting point, which remained constant at 131° C.

A sample of this purified furoic acid exposed to the regular laboratory conditions for 3 months showed a gain of 0.04 per cent moisture, indicating that it was slightly hygroscopic, but this slight trace of water was readily removed by careful fusion.

The sodium hydroxide solution used was prepared free from carbonates. It was carefully protected from the carbon dioxide of the air by guard tubes and all titrations were performed on the same day in order to avoid possible errors in the titrations due to contamination by carbonates. The apparatus in which the titrations were performed was that of Jackson.[1]

Standardization of Sodium Hydroxide by Benzoic Acid

The first step was to standardize the sodium hydroxide solution by the use of benzoic acid which was fused and cooled before using. The titration was performed according to the directions in Certificate No. 39d for benzoic acid, U. S. Bureau of Standards, using the Jackson titrating apparatus. Various weighings of benzoic acid were taken, 3 drops of a 1 per cent solution of phenolphthalein were added, and the solution was titrated with the approximately 0.1 *N* alkali. The results obtained are shown in Table I.

Table I. Benzoic Acid

(99.98 per cent pure Bureau of Standards Sample No. 39d)

No.	Weight of Sample	NaOH Used	Relative Normality	Corrected Normality
	Gram	*Cc.*		
1	0.3241	25.49	0.10417	0.10415
2	0.3419	26.90	0.10414	0.10411
3	0.2551	20.07	0.10414	0.10411
4	0.3133	24.64	0.10418	0.10415
5	0.2981	23.44	0.10420	0.10417
6	0.3091	24.32	0.10413	0.10410
7	0.2446	19.24	0.10416	0.10413
		Mean of seven determinations		0.10413

Standardization by Potassium Phthalate

The second step was to repeat the standardization by the use of potassium acid phthalate. These titrations were performed as described in Certificate No. 84, U. S. Bureau of Standards, and the results obtained are recorded in Table II.

Table II. Potassium Acid Phthalate

(99.97 per cent pure Bureau of Standards Sample No. 84)

No.	Weight of Sample	NaOH Used	Relative Normality	Corrected Normality
	Gram	*Cc.*		
1	0.2122	9.98	0.10415	0.10411
2	0.2319	10.90	0.10421	0.10417
3	0.3115	14.64	0.10422	0.10418
4	0.2535	11.92	0.10417	0.10413
5	0.2242	10.54	0.10419	0.10415
6	0.3575	16.80	0.10423	0.10419
		Mean of six determinations		0.10415

Standardization of Furoic Acid

Before using, the purified furoic acid was fused in a covered platinum dish over an air bath. The temperature during the fusion did not exceed 142° C. Upon completion of the fusion the acid was cooled in a desiccator. Various weighings were transferred into the titrating apparatus, 25 to 50 cc. of previously boiled distilled water were added, and the apparatus was swept free from carbon dioxide. The sample was allowed to stand until the acid had dissolved and then titrated. The results are shown in Table III.

Table III. Furoic Acid

No.	Weight of Sample	NaOH Used	Normality
	Gram	*Cc.*	
1	0.2927	25.08	0.10417
2	0.2033	17.43	0.10411
3	0.4754	40.73	0.10418
4	0.3000	25.72	0.10411
5	0.3321	28.45	0.10419
6	0.2862	24.52	0.10418
		Mean of six determinations	0.10415

[1] Jackson, J., *J. Soc. Chem. Ind.*, **53**, 36 (1934).

Conclusion

The normalities obtained by the use of benzoic acid and potassium acid phthalate, respectively, show that on the basis of these titrations furoic acid has a purity of 100 per cent and a neutralizing power almost equivalent to benzoic acid. There is no justification for carrying the normality beyond the fourth decimal place without such precautions as correction of weights to *vacuo* and the use of weight burets; however, these figures were carried out to the fifth decimal place to show the relative purity of furoic acid and the close agreement of the results obtained. They indicate that furoic acid can be employed as a standard because of the following advantages: ease of obtaining the acid in a fairly high state of purity, coupled with ease of purification; solubility in water, which is the chief advantage over benzoic acid, as benzoic acid requires the use of alcohol to effect solution; its fairly high molecular weight, permitting large samples; and finally its stability and lack of appreciable hygroscopicity.

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Mixed Perchloric and Sulfuric Acids

II. Potassium Ferro- and Ferricyanides as Reference Standards in the Evaluation of Titanous Solutions

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Potassium ferricyanide as a reference standard (*1*, *2*) is the only practical example of a salt of ferric iron suitable for the evaluation of reducing solutions. Its reaction with potassium iodide in acid solution, with or without the addition of zinc, for the liberation of iodine followed by reaction with sodium thiosulfate is an important procedure of iodometry. Potassium ferrocyanide trihydrate can be used as a reference standard for the same purpose. In this case (*4*) a weighed quantity of the salt is oxidized with a slight excess of potassium permanganate. Potassium bromide is added to remove the excess permanganate, followed by hydrazine sulfate to remove bromine. The ferricyanide thus formed is used to liberate iodine from potassium iodide. Potassium ferrocyanide has been used in the direct standardization of potassium permanganate (*3*) in sulfuric acid solution, but the reaction for this purpose has no advantage over other methods except the high equivalent weight, and there are several disadvantages.

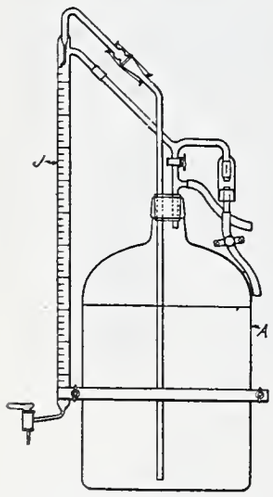

Figure 1. Diagram of Apparatus

The ferro- or ferricyanide is decomposed by digestion with mixtures of perchloric and sulfuric acid or by perchloric acid alone. The process serves, therefore, for the determination of ferro- and ferricyanides and has the distinct advantage that insoluble salts can be determined without previous liberation of the iron by digestion with sodium carbonate. Finally, the new process simplifies the use of titanous solutions as a laboratory volumetric reagent, an influence favoring its more general application.

Apparatus

The automatic storage bottle and buret delivery assembly with an atmosphere of hydrogen as described by Zintl and Rienäcker (*6*) was employed, somewhat modified in accordance with the drawing of Figure 1. The storage bottle, *A*, was of 14 liters capacity and buret *J* a 50-ml. U. S. Bureau of Standards calibrated goose-neck buret modified as shown.

The titration flask is shown in Figure 2. A 300-ml. Erlenmeyer flask, *A*, has the insealed side arm, *B*, of 8-mm. glass tubing terminating on the inside at the bottom of the flask. A 2-inch (5-cm.) extension outside is for connection to a source of carbon dioxide or hydrogen gas. The titration head, *C*, is made from a 100-ml. beaker with a 12-mm. neck sealed in the bottom at *D* for insertion of the buret tip and side arm *E* for washing the inside walls of the reaction flask.

The digestion of samples of potassium ferro- and ferricyanides with either perchloric acid or mixtures of perchloric and sulfuric acids to destroy organic matter required that a cover to the flask be employed to prevent loss by spray. An inverted crucible cover was not satisfactory since drops of cold acid collected on the projection of these lids and, upon dropping into the hot acid of the solution below, caused violent spattering. This difficulty was corrected by a chestnut-shaped cover, *F*, made from short sections of 35-mm. tubing closed flat at one end and with an extension as shown to make contact with the inside top of the 300-ml. Erlenmeyer flasks used for the digestions. Drops of condensed acid from the under side of the cover return to the flask down the side walls and the difficulty of spattering is eliminated.

Materials

Potassium Ferricyanide. As ordinarily purchased from stock, this reagent was found to be sufficiently pure. It was ground to a fine powder and dried at 135° to 140° C.

Potassium Ferrocyanide. Stock preparations were found to be of a high degree of purity but of indefinite degrees of hydration. The sample from stock was therefore dried over anhydrone at 135° to 140° C. to form the anhydrous salt, or, in some cases, it was found necessary to purify by recrystallization with subsequent drying to the anhydrous form.

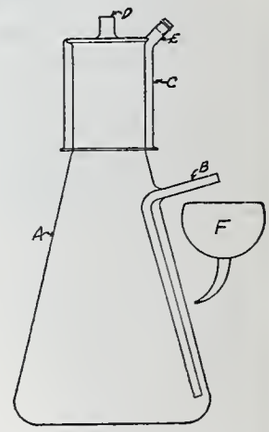

Figure 2. Titration Flask and Protection Head

Titanous Chloride. A stock solution of 20 per cent titanous chloride in hydrochloric acid was diluted to the desired strength after the addition of hydrochloric acid. It was not tested for ferrous iron since with the methods to be employed this impurity has no influence.

Perchloric Acid. The 70 to 72 per cent, c. p. (sp. gr. 1.67) acid free from iron was diluted to 60 per cent (sp. gr. 1.54) for oxidation of ferro- and ferricyanides if used alone. The full strength was used if the oxidations were to be made with the addition of sulfuric acid.

Sulfuric Acid. The regular stock 96 per cent (sp. gr. 1.84) acid was diluted to 75 per cent strength (sp. gr. 1.675).

Perchloric and Sulfuric Acid Mixture. One part by volume of 70 to 72 per cent perchloric acid was mixed with five parts by volume of 75 per cent sulfuric acid.

Ammonium Thiocyanate. A 10 per cent solution of c. p. stock crystals which gave a colorless solution was prepared.

Ferric Alum and Potassium Permanganate. Solutions of approximately 0.1 N strength were prepared in the usual manner for stock reagents.

Sodium Oxalate. Bureau of Standards sodium oxalate; dried at 100° C.

Standardization of Solutions

Potassium Permanganate. Weighed samples of sodium oxalate were dissolved in 15 to 20 per cent sulfuric acid and titrated hot by the addition of the potassium permanganate from weighing burets. The results of the standardization were as follows:

	1	2	3	4	5
Sample of $Na_2C_2O_4$, gram	0.1934	0.2306	0.2257	0.1902	0.1966
Weight of $KMnO_4$ solution required, grams	35.318	40.256	40.3525	34.656	35.823
N $Na_2C_2O_4$ per gram of $KMnO_4$, ml.	0.08174	0.08166	0.08183	0.08192	0.08192

Av. 0.08182 ml. of N $KMnO_4$ per gram of solution.

Ferric Alum Solution. Weighed portions of the ferric alum solution containing 5 per cent of free sulfuric acid were reduced by a Jones reductor and the ferrous iron titrated using standard potassium permanganate. The solutions were reduced in the cold and titrated with potassium permanganate after the addition of sufficient phosphoric acid to decolorize the iron after oxidation. Weighing burets were used for both solutions. The results follow.

	1	2	3	4
Ferric alum solution, grams	43.013	44.342	44.678	45.1415
$KMnO_4$ solution, grams	74.490	73.533	73.996	74.922
N $Fe_2(SO_4)_3$ per gram of solution, ml.	0.13557	0.13585	0.13568	0.13596

Av. 0.1358 ml. of N $Fe_2(SO_4)_3$ per gram of solution.

Titanous Chloride Solution. Weighed portions of standard ferric alum were taken using weighing burets. The samples were treated with 10 ml. of ammonium thiocyanate and titrated with titanous chloride, using the apparatus described and a stream of carbon dioxide. The reagent was added dropwise at the end of the reaction to avoid overtitration as a result of the slow reaction velocity at the end point. Titration was made at room temperature following the directions of Thornton and Chapman (*5*). Hydrogen gas can be used in place of carbon dioxide as shown by the results of cases 1 and 2 following.

	1	2	3	4	5	6
Ferric alum solution, grams	12.0657	9.8760	10.6586	9.6642	9.6783	9.7577
Titanous chloride solution, ml.	59.61	47.85	51.76	46.90	47.05	47.30
Normality of titanous chloride	0.02749	0.02796	0.02796	0.02798	0.02793	0.02801

Av. (results 2 to 5 incl.): titanous chloride = 0.02796 N.

A second solution of titanous chloride was similarly prepared and stored under hydrogen. It was found to have the value 0.0550 N. It was used to check the efficiency of the hydrogen storage bottle described below.

Oxidation of Potassium Ferro- and Ferricyanides Using Perchloric and Sulfuric Acids

Samples of anhydrous potassium ferro- or ferricyanides of approximately 400 mg. were weighed from a glass-stoppered bottle into clean, dry 300-ml. Erlenmeyer flasks. Perchloric acid (10 ml. of 60 per cent) was added and each flask covered with the cover glasses previously described and heated on the hot plate to just below the boiling temperature for 30 minutes. The reaction mixture first precipitates potassium perchlorate and, as the temperature rises, the yellow solution due to the ferro- or ferricyanide turns dark blue. The decomposition products of this color then turn brown and some spray forms as a result of the oxidation of a small amount of deposited colloidal carbon to carbon dioxide. The digestion need not be done in a draft hood. As the heating is continued, the 60 per cent acid concentrates to 70 to 72 per cent strength and the solution gradually turns light yellow as chlorine is formed from the decomposition of the hot, concentrated perchloric acid. The digested solution, after this 30-minute treatment, is cooled to approximately 100° C. and 20 ml. of water are added. The flask contents are gently boiled for 2 minutes to expel chlorine, cooled, and transferred to the titration vessel and diluted to 100 ml. after the addition of 10 ml. of 10 per cent ammonium thiocyanate. Carbon dioxide is passed in for a few minutes, and the solution titrated with titanous chloride solution in a current of carbon dioxide. The last few drops of the reducing agent are added with a time lapse of one minute between drops.

The required amount of perchloric acid, if thought to involve excessive cost, can be reduced greatly by using an oxidation mixture of sulfuric acid to which is added a small portion of perchloric acid. The boiling point of the mixed acids is higher because of the sulfuric acid present and the oxidation is somewhat more rapid, but the formation of insoluble ferric sulfate requires a little more heating after digestion and dilution to dissolve the ferric sulfate which has been partially dehydrated. The heating does not completely dehydrate the ferric sulfate and it is fairly easily dissolved upon dilution. Sulfuric acid alone for the process was found to be unsatisfactory, the decomposition always being incomplete after 30 minutes' digestion. If the cost is not considered, the perchloric acid alone is to be preferred.

Standardization of Titanous Chloride Using Potassium Ferricyanide

A sample of J. T. Baker's potassium ferricyanide was pulverized and dried 12 hours at 100° C. Weighed samples were digested using 2 ml. of 70–72 per cent perchloric acid plus 8 ml. of 75 per cent sulfuric acid for 30 minutes. The resulting mixture was diluted with a little water and the chlorine expelled by gentle boiling. The samples were diluted to 80–100 ml. and titrated with titanous chloride as previously described. The resultant values are found in Table I.

Table I. $K_3Fe(CN)_6$ as Primary Standard for Evaluation of Titanous Chloride

$K_3Fe(CN)_6$	Volume of Ti^{+++} Solution	Normality of Ti^{+++} Found	Fe^{+++} Present	Fe^{+++} Found	Error Fe
Gram	*Ml.*		*Mg.*	*Mg.*	*Mg.*
0.4926	53.33	0.02806	83.56	83.26	+0.30
0.4842	52.69	0.02792	82.13	82.26	−0.13
0.3967	43.07	0.02798	67.29	67.24	+0.05
0.4463	48.45	0.02798	75.71	75.64	+0.07
0.4633	50.25	0.02801	78.59	78.45	+0.14
0.4087	44.42	0.02795	69.33	69.35	−0.02
		Av. 0.02798			+0.07

Av. value of $TiCl_3$ from previous standardization = 0.02796.

It will be seen from Table I that the standardization of a titanous solution by the new process gives an average accuracy of one part in one thousand using potassium ferricyanide without further purification. The high equivalent weight, 329.19, requires 400 to 500 mg. for each 44 to 54 ml. of 0.028 N titanous solution. The process is therefore admirably suited to the standardization of weak solutions which are most frequently employed in titanometry.

Standardization of Titanous Chloride Using Potassium Ferrocyanide

A sample of J. T. Baker's hydrated potassium ferrocyanide was recrystallized from water, pulverized, and dried 12 hours

at 135° to 140° C. over anhydrone. Weighed samples of this product were used to standardize the titanium solution as described in the case of the ferricyanide with the results found in Table II.

TABLE II. $K_4Fe(CN)_6$ (ANHYDROUS) AS PRIMARY STANDARD FOR EVALUATION OF TITANOUS SOLUTIONS

(Conditions same as in Table I)

$K_4Fe(CN)_6$	Volume of Ti^{+++} Solution	Normality of Ti^{+++} Found	Fe Present	Fe Found	Error Fe
Gram	*Ml.*		*Mg.*	*Mg.*	*Mg.*
0.4199	40.80	0.02795	63.66	63.70	−0.04
0.4173	40.66	0.02787	63.27	63.48	−0.21
0.3882	37.90	0.02793	58.86	59.17	−0.31
0.4215	41.15	0.02781	63.91	64.25	−0.34
0.4070	39.43	0.02803	61.71	61.56	−0.15
		Av. 0.02792			−0.21

It will be observed that results are obtained which, while not quite as satisfactory as those obtained using potassium ferricyanide, are well within the range of ordinary error—4 parts in 2800 or approximately 0.15 per cent.

INFLUENCE OF TIME UPON REDUCING VALUE OF TITANOUS CHLORIDE

Two solutions of titanous chloride stored under hydrogen in the apparatus described in Figure 1 were tested. The determinations of the first solution were made with potassium ferricyanide by the process described above but without the use of a titration head or stream of carbon dioxide during titration. The results with the second solution were obtained using the titration head and a stream of carbon dioxide. In all cases the standardization was carried out in duplicate or triplicate. The results are found in Table III. The value for the second solution at the beginning of the storage period was obtained, as previously described, using ferric alum standardized by permanganate through sodium oxalate.

TABLE III. INFLUENCE OF TIME OF STORAGE UNDER HYDROGEN UPON REDUCING STRENGTH OF TITANOUS CHLORIDE

Time stored, days	1	2	3	4	5	8	15
Solution 1, normality	0.0551	0.0550	0.0550	0.0550	0.0550	0.0549	
Solution 2, normality	0.02796	....	....	....	....	....	0.02796

No hazardous reactions are described in connection with this paper.

SUMMARY

Potassium ferricyanide has been shown to be an accurate primary standard for ferric iron after oxidation with perchloric acid or perchloric acid and sulfuric acid to liberate its iron either as ferric perchlorate or as the perchlorate plus sulfate. The ferricyanide is stable at 140° C. for dehydration.

Potassium ferrocyanide trihydrate can be dried at 140° C. to form the anhydrous salt and serves as a substitute for potassium ferricyanide.

Potassium ferri- and ferrocyanides have been shown to be capable of standardizing solutions of titanous chloride with an accuracy of one part in one thousand.

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Estimation of Methyl Salicylate, Menthol, and Camphor in Mixtures

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THE literature dealing with the estimation of methyl salicylate, menthol, and camphor in medicinal preparations discloses the difficulties of obtaining accurate results. Menthol and camphor present particular problems owing to their volatility even at room temperature. Methods have been published for the analysis of substances containing one or two of these three ingredients, but none was found which involved the estimation of all three in one sample.

Methyl salicylate is usually determined by the use of alcoholic potassium hydroxide to saponify the ester, the quantity used being determined by titrating the excess alkali (*16*). When other saponifiable substances are present, the salicylic acid formed by saponification is sometimes extracted with ether (*9*).

Menthol, while more difficult to determine, can be satisfactorily estimated by itself by acetylation (*6, 8, 17*).

Camphor in substantial amounts is estimated by polarization in alcohol (*18, 20*) or benzene (*5*) with satisfactory accuracy. In small amounts it cannot be determined with a high degree of accuracy by known methods. Reported methods include precipitation and gravimetric estimation as semicarbazone (*1*), salol camphor (*15*), and the oxime (*2, 14*). Estimation by loss on evaporation from a nonvolatile base is inaccurate if the base is oxidizable (*19*).

Other methods are extraction with carbon tetrachloride and evaporation of the solvent in an atmosphere saturated with camphor (*7*), extraction from aqueous salt solution (*3, 10*) with ether, and extraction from aqueous solution with petroleum ether (*12*). Estimation of camphor by its effect on the surface tension of an aqueous solution has also been proposed (*4, 13*). Results 10 per cent low for camphor are reported in extraction of menthol–methyl salicylate mixtures followed by determination of the methyl salicylate (*11*).

An effort was made to select from these methods those which could be suitably combined in a procedure for analysis of commercial products. The mixtures to which the method was applied were analgesic balms made by well-known manufacturers. These consist of a base of lanolin, petrolatum, or gum solution, in which the methyl salicylate, menthol, and camphor have been incorporated.

PROCEDURE

Weigh about 20 grams of the substance into a flask and steam-distill, using an efficient condenser, till no more oily matter comes over. Usually about 500 cc. of distillate are sufficient.

Rinse the condensing system with 50 cc. of ether and add this to the distillate in a separatory funnel. Extract the distillate with this 50-cc. portion of ether. Repeat with another 50-cc. portion of ether. The aqueous layer still contains some menthol and camphor in solution, because of the solubility of ether in

water. Saturate the solution with salt and extract with two more 50-cc. portions of ether. Filter the combined ether extracts through a dry filter paper into a weighed narrow-necked glass-stoppered flask. An iodine flask is suitable. Evaporate the bulk of the ether on a water bath. Remove the remaining ether under a moderate vacuum at room temperature. This minimizes loss of menthol and camphor due to volatilization; 30 minutes to 1 hour in the vacuum desiccator is usually sufficient. As a check on later results weigh the flask and extract. This gives the combined weights of methyl salicylate, menthol, camphor, and any oil that has been distilled over from the base.

Add 25 cc. of approximately N potassium hydroxide solution in absolute methyl alcohol to the flask, or to a portion weighed out therefrom if the amount is large. Reflux for 2 hours. To minimize loss during subsequent evaporation it is advisable to keep the volume of alkali solution added low. For this reason N instead of 0.5 N potassium hydroxide is used and the lower-boiling methyl alcohol is used instead of ethyl alcohol. After refluxing, evaporate the bulk of the methyl alcohol on a water bath, dilute with 50 cc. of water, and titrate with 0.5 N hydrochloric acid. Run a blank equal to the amount of alcoholic potassium hydroxide used and titrate. The difference gives the potassium hydroxide used in saponifying the methyl salicylate. Then

$$\text{cc. } 0.5\ N \text{ KOH used} \times 0.07605 \times \frac{100}{\text{wt. of sample}} = \text{per cent of methyl salicylate}$$

After titration transfer the contents of the flask with water to a separatory funnel. Rinse the flask with ether and extract the solution twice with 50 cc. of ether. Then saturate with salt and extract with two more 50-cc. portions of ether as before. Filter through dry filter paper into a dried and weighed narrow-neck, glass-stoppered flask and evaporate off most of the ether on a water bath. As previously, finish evaporation of the ether in a moderate vacuum at room temperature and weigh. This weight gives a check on the amount of menthol and camphor present, with possibly a small amount of oil distilled over from the base. The loss in weight should check with the amount of methyl salicylate determined by saponification.

Add to the flask 10 cc. of acetic anhydride and 1 gram of anhydrous sodium acetate. Reflux gently for 1 hour, cool, and wash into a separatory funnel. Wash two or three times with water, being careful not to shake too vigorously. The addition of salt will assist in preventing formation of emulsions. Then wash with very dilute sodium hydroxide or with 2 N sodium carbonate until just alkaline, and finally wash once with distilled water. Drain well and transfer by washing with neutralized absolute methyl alcohol into a dry flask. It is not necessary to perform the tedious drying with calcium chloride usually recommended in the acetylation method for menthol. Saponify the acetylated menthol by heating gently under reflux for 1 hour with 25 cc. of 1 N potassium hydroxide in absolute methyl alcohol. Treat a blank of the alcoholic alkali similarly. Cool, dilute with water, and titrate the sample and blank with 0.5 N hydrochloric acid. The difference is due to alkali used in saponification of acetylated menthol. Calculate as follows:

$$\text{cc. } 0.5\ N \text{ KOH used} \times 0.0781 \times \frac{100}{\text{wt. of sample}} = \text{per cent of menthol}$$

Subtracting this from the previous weight gives the percentage of camphor plus oil.

To obtain the amount of camphor, extract the contents of the flasks as before with ether. Evaporate the ether in a weighed crystallizing dish on a water bath, and weigh to obtain a value for menthol and camphor. After all the ether is gone, place the dish in an oven at 110° C. Menthol and camphor are volatilized. The residue is oil from the base which was volatile with steam. Calculation, allowing for the menthol determined by saponification, gives the amount of camphor present. An error will be introduced if the sample contains drying oil.

In actual practice it has been found that the amount of oil from the base distilled over was negligible and need only be taken into account for very accurate work. For routine determinations it is therefore not necessary to perform the last extraction and the volatilization of the menthol and camphor.

The method was applied to a synthetic sample with the following results.

	Added	Found
	%	%
Lanoline	76	...
White petrolatum	10	...
Methyl salicylate	10	10.05
Menthol	2	1.87
Camphor	2	2.18

The accuracy of the technic is also confirmed by satisfactory checks when applied to commercial samples, and agreement with the known composition of commercial products.

Discussion

While the above method is necessarily rather long, it is not involved and can be performed in a surprisingly short time. The three ingredients can be determined on the one sample. The base itself can be identified and determined on the residue after steam distillation of the same sample. The objection to using ether as an extracting agent, owing to its solubility in water with consequent solubility of menthol and camphor, is overcome by the use of salt. Ether is the best extraction medium because of its very low boiling point.

By employing the low-boiling methyl alcohol for the saponifications it is possible to evaporate without substantial loss of menthol and camphor. Finally, the troublesome drying of the acetylated menthol is eliminated.

Summary

Available methods for estimation of methyl salicylate, menthol, and camphor do not include mixtures such as occur in analgesic balms. Methyl salicylate may be determined by saponification and checked by the loss in weight of sample resulting. Camphor is then determined by the acetylation method. Camphor and menthol are estimated by volatilization and menthol then obtained by difference. A synthetic sample shows a high degree of accuracy for methyl salicylate and accuracy within 10 per cent for camphor and for menthol.

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Deterioration of Eggs in Storage. The secret of why storage eggs compare unfavorably with fresh eggs has been revealed by scientists of the Department of Agriculture, who have found that an egg deteriorates in storage because it is digesting itself. For years food chemists have suspected that trypsin, one of the enzymes present in the pancreatic juice of the human body, was present in egg white. Recent experiments have shown the existence of this enzyme in egg white.

The search for trypsin in egg white was hindered by the presence of a substance which inhibits further action of the enzyme. Consequently, tests of mixed thick and thin egg white have failed to show the presence of trypsin.

Rapid Method for Determination of Small Amounts of Arsenic

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A method is given for the determination of arsenic by estimating the evolved arsine deposited upon a mercuric-bromide-impregnated diaphragm. It is applicable for estimating minute quantities of arsenic in the presence of impurities such as iron, tin, antimony, or reducible sulfur and phosphorus compounds. Modifying the procedure somewhat makes it possible to determine the arsenic content of many products using an undigested sample.

THE method is essentially a modified Gutzeit procedure, except that the arsine is liberated from the sample in a manner similar to that employed by Smith (*15*) and Taber (*17*) but using smaller quantities. Taber modified Smith's procedure by adopting a larger generator flask to accommodate a larger volume of liquid and fitting to it a condenser so that heat could be applied to the flask to secure proper reduction of the arsenic and a vigorous ebullition of gas. The estimation of arsenic by Taber's distillation method was based upon an iodine titration of the reaction products formed when arsine is passed into mercuric chloride solution.

The method described in this paper differs from that of Taber and the official Gutzeit method in that the evolved arsine is impinged upon an impregnated mercuric bromide diaphragm securely held between two ground-glass joints. The colored disks are then developed in a solution of iodide (*1, 7*) and compared with standards. Earlier workers have employed the principle of stain deposition upon a sensitized paper disk (*2, 3, 4, 11, 12*), but the sensitizing solution used was mercuric chloride. Various devices for securing the diaphragm in place have also been suggested (*6, 8, 9, 13, 14, 16, 18, 19*); some of these were unsatisfactory because they did not enable the operator to obtain a stain with a sharply defined boundary, and others were subject to criticism for reasons related to simplicity of design or ease of manipulation.

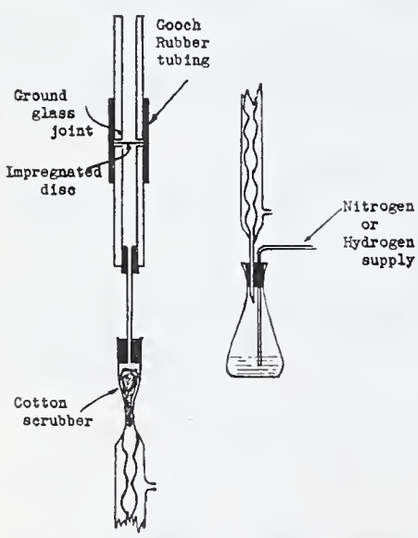

Figure 1. Apparatus for Arsenic Determination

For minute amounts of arsenic the method is especially applicable, as the entire digest of a sample can be used. With a disk 20 mm. in diameter 0.001 to 0.040 mg. of arsenic trioxide can be directly determined. The analysis can be made in the presence of impurities such as iron, tin, antimony, or reducible sulfur or phosphorus compounds, which tend to affect the evolution rate of arsine or to deposit interfering stains on the mercuric bromide strips used in the regular Gutzeit method.

Reagents

Hydrochloric Acid. Make up 50 cc. of 35 per cent arsenic-free hydrochloric acid to 100 cc. with water.

Stannous Chloride Solution. Dissolve 40 grams of arsenic-free $SnCl_2 \cdot H_2O$ in concentrated hydrochloric acid and make up to 100 cc. with the same strength acid.

Mercuric Bromide Paper. Carefully select filter sheets, similar to S & S No. 589 black ribbon paper, for weight and texture, and soak one hour in a saturated alcoholic solution of mercuric bromide. After sensitizing, remove sheets and dry by means of an air blast, and cut in disks of the same diameter as the diaphragm tube. Avoid touching the sensitized disks with the hands as far as possible. Disks should not be used when more than 5 or 6 days old.

Zinc. Cut arsenic-free zinc in pieces about 1 cm. in length (approximately 5 grams). Activate the pieces by covering with hydrochloric acid (1 + 3) containing about 2 cc. of special stannous chloride solution for each 100 cc. of acid. Allow the action to continue for 15 minutes and wash well with distilled water.

Potassium Iodide Solution. Dissolve 15 grams of potassium iodide in water and dilute to 100 cc.

Ferrous Ammonium Sulfate. Use this substance or ferrous sulfate crystals free from arsenic.

Cuprous Chloride Solution. Dissolve 15 grams of cuprous chloride in 100 cc. of 1 to 1 hydrochloric acid.

Cadmium Iodide Solution. Dissolve 20 grams of cadmium iodide in water and dilute to 100 cc.

Standard Arsenic Solution. Dissolve 1 gram of arsenic trioxide in 25 cc. of 20 per cent sodium hydroxide. Saturate the solution with carbon dioxide and dilute to 1 liter with recently boiled water. One cc. of this solution contains 1 mg. of arsenic trioxide. Dilute 40 cc. of this solution to 1 liter, diluting 50 cc. of the resulting solution to 1 liter. One cc. of this latter solution contains 0.002 mg. of arsenic trioxide and is used to prepare standard stains. Prepare fresh dilute solutions at frequent intervals.

Apparatus and Procedure

Use an Erlenmeyer flask connected by a two-hole stopper to a Liebig or Allihn condenser. A gas such as nitrogen or hydrogen is introduced through a tube extending below the surface of the contents of the flask. The upper end of the condenser is packed with absorbent cotton, the lower half of which is saturated with the cuprous chloride solution which acts as a scrubber to remove impurities, such as phosphine, stibine (*10*), and hydrogen sulfide, from the evolved arsine. A chamber having a diameter that will accommodate a sensitized diaphragm of a size sufficient to combine with all the arsine is fitted to the condenser. The chamber consists of two thick-walled tubes of the same diameter with ground-glass joints held together by an outside sleeve of Gooch rubber tubing. The impregnated paper is fitted between the two ground joints as pictured in Figure 1.

An aliquot obtained from a sample digested with sulfuric and nitric acid in the usual manner (or the entire digestion in case of small amounts) is placed in a 1000-cc. Erlenmeyer flask with enough distilled water to make about 200 cc. of solution. Then 2 to 3 grams of solid ferrous ammonium sulfate or ferrous sulfate, 10 to 15 drops of stannous chloride solution and 50 cc. of 1 to 1 hydrochloric acid are added. Just before connecting to the condenser, introduce two or three pieces of activated zinc. A continual stream of nitrogen is kept flowing through the system to carry all traces of evolved arsine through the scrubber cotton to the paper diaphragm impregnated with mercuric bromide. The contents of the flask are boiled until all the arsine is evolved, which usually requires about 15 minutes. When the reaction is complete, the disk is removed and developed in cadmium iodide solution. This fixes the stain more permanently to light and water than does potassium iodide and changes the color from yellow to brown. The disk is allowed to remain in the iodide solution until all traces of red mercuric iodide, which immediately forms, have been dissolved. After prolonged use, the cadmium

iodide solution turns yellow from the accumulation of complex cadmium mercuric iodides and should be replaced by fresh reagent. The excess reagent is removed from the disk by a water wash followed by a rinse with alcohol, and the disk is then dried between blotters. When dry the stains are compared with standards. The standards are prepared in a similar manner to the unknowns in steps of 0.0025 mg. of arsenic trioxide, keeping them free from excess light exposure. The stains have a tendency to bleach slightly with age and it is desirable to prepare fresh standards frequently, especially in the approximate range of the unknown.

With some modifications the method is applicable to the undigested material, thus shortening the total time of an arsenic determination to 15 to 30 minutes and eliminating the costly procedure of digestion with nitric and sulfuric acids.

From 5 to 100 grams of the undigested sample may be placed directly in the 1000-cc. Erlenmeyer flask together with 100 cc. of 1 to 1 hydrochloric acid, 1 to 2 cc. of stannous chloride solution, 15 cc. of potassium iodide solution, and 1 to 2 grams of solid ferrous sulfate. The activated zinc (three or four pieces) is added, and the flask immediately connected to the condenser unit. The reaction is usually complete after 15 minutes of boiling except that, when using large amounts of sample, a somewhat longer time may be necessary to evolve all the arsine. The scrubber cotton should be saturated with a 15 per cent solution of cuprous chloride in 1 to 1 hydrochloric acid to remove hydrogen sulfide, phosphine, and stibine, if present. In case these gases have not been efficiently removed, the yellow stain imparted to the disk is not changed to brown when immersed in the cadmium iodide solution. When using large samples of some products that contain considerable reducible sulfur or phosphorus compounds, the scrubber cotton may not remove all impurities, and a preliminary treatment is necessary. The sample is heated a short time with an alkaline solution, after which it is slightly acidified with hydrochloric acid and the excess sulfide removed by boiling. The remaining sulfur and reduced phosphorus compounds are oxidized with bromine water, and then the bromine is removed by boiling before adding the sample to the reaction flask.

Table I. Recovery of Added Inorganic Arsenic from Undigested Food Products

(20-mm. disk)

Samples	As_2O_3-Free Product	Weight of Sample	Added As_2O_3	Recovered As_2O_3[a]
		Grams	*Mg.*	*Mg.*
4	Apple sauce	20	0.010	0.008–0.011
3	Apple sauce	20	0.020	0.018–0.021
4	Apple butter	20	0.005	0.004–0.006
4	Apple butter	20	0.0075	0.0075–0.009
4	Apple butter	50	0.010	0.009–0.011
15	Canned peaches	50	0.010	0.0075–0.010
1	Canned pears	50	0.010	0.010
2	Canned cherries	50	0.005	0.004–0.005
4	Canned cherries	50	0.010	0.008–0.010
2	Canned apricots	50	0.010	0.009–0.010
3	Canned sauerkraut	20	0.010	0.009–0.011
2	Canned celery	20	0.010	0.010
1	Canned spinach	20	0.010	0.009
1	Apple cider	50 cc.	0.010	0.010
1	Apple cider	50 cc.	0.020	0.019
10	Shrimp[b]	10	...	Trace[b]
5	Shrimp	10	0.005	0.005–0.006
5	Shrimp	10	0.010	0.010–0.012
2	Shrimp	10	0.020	0.018–0.022

[a] Maximum spread of results.
[b] These samples all contained arsenic originally which could not be recovered by the disk method except after complete digestion with nitric and sulfuric acids.

Table II. Tests on Lye-Peeled Peaches

Sample	Gutzeit Method	Disk Method	Sample	Gutzeit Method	Disk Method
	Mg./gram	*Mg./gram*		*Mg./gram*	*Mg./gram*
83	0.00010	0.00014	52	0.00010	0.00017
173	0.00021	0.00028	89	0.00015	0.00036
130	0.00015	0.00017	54	0.00014	0.00028
85	0.00014	0.00034	136	0.00011	0.00017
175	0.00028	0.00029	137	0.00011	0.00007
132	0.00007	0.00014	183	0.00004	0.00004

Discussion of Results

Known amounts of added inorganic arsenic were directly recovered from undigested material in such products as fruits, apple sauce, apple butter, cider, sauerkraut, celery, and other vegetables. However, in the case of marine products, such as shrimp, it was not possible to determine

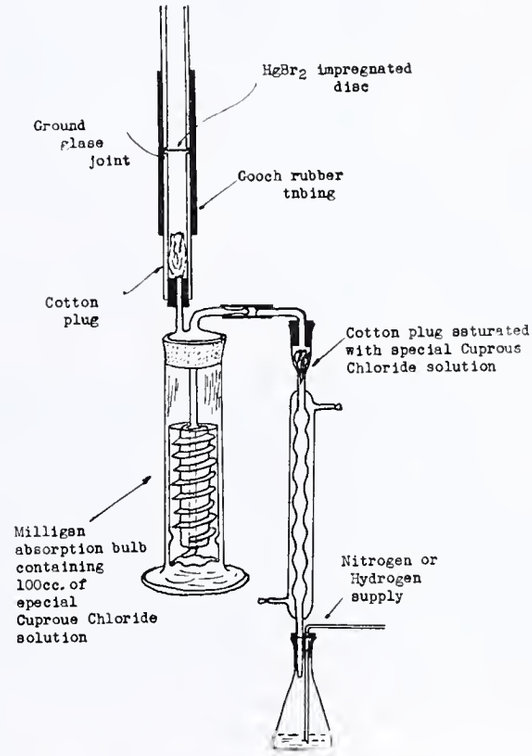

Figure 2. Special Apparatus for Arsenic Determination

the original arsenic content without first thoroughly digesting the sample with nitric and sulfuric acids, although complete recovery was made of inorganic arsenic added to undigested samples of macerated shrimps previously found to give negative results for arsenic by the disk method (Table I). Determinations made of the original arsenic content of various undigested fruit and vegetable products were found to be in good agreement with those obtained by the Gutzeit method on the same samples after digestion. The presence of such substances as waxes, casein binders, oils, soaps, and nicotine bases, which are used in various spray mixtures, were found to be without effect in the determination. One set of data obtained on lye-peeled peaches which had been heavily sprayed with lead arsenate in plot tests made by representatives of the Department of Agriculture of the State of California (*5*) is shown in Table II. The disk method was employed on 50-gram samples of the raw product using a 15-mm. disk, and check analyses were made by the Gutzeit method on one-fifth aliquots of a 210-gram sample digested with nitric and sulfuric acids.

After using the disk method in this laboratory over the period of a year for the analysis of various products, the

Blank | 0.00125 mg. | 0.0025 mg. | 0.005 mg. | 0.0075 mg. | 0.010 mg. | 0.015 mg. | 0.020 mg. | 0.025 mg. | 0.030 mg. | 0.040 mg.

Standard Arsenic Stains

(20-mm. disk)

method was submitted to an industrial laboratory for use. Using 20-gram samples of undigested material in the disk method with 20-mm. diaphragms, the variation they obtained on fifty-four samples of apple butter (ranging in arsenic trioxide content from 0.1 to 3.0 p. p. m.) compared to the Gutzeit determination run on a digested sample is shown in Table III.

Table III. Comparison of Gutzeit and Disk Methods

Samples	Deviation from Gutzeit	Samples	Deviation from Gutzeit
	P. p. m. As_2O_3		*P. p. m.* As_2O_3
1	+0.3	14	0
8	+0.2	12	−0.1
18	+0.1	1	−0.2

Deviation from Gutzeit = v
No. of samples = D

$$\text{Mean} = \frac{\Sigma v}{n} = +0.04 \text{ p. p. m.}$$

$$\text{Standard deviation} = \sigma = \sqrt{\frac{\Sigma v^2}{D}} = 0.12 \text{ p. p. m.}$$

Probable error of a single determination = 0.6745 σ = ±0.08 p. p. m. = ±0.0016 mg. As_2O_3

Small amounts of arsenic were quantitatively removed in the presence of relatively large amounts of antimony. A special absorption train (Figure 2) is necessary, however, when more than 30 mg. of antimony are present, as the single cuprous-chloride-saturated cotton plug is not efficient above that range. Excessive amounts of reducible phosphorus and sulfur compounds also require the special train unless they are previously oxidized with bromine water.

Some examples of the recoveries of added arsenic in the presence of arsenic-free contaminants appear in Table IV.

Table IV. Recovery of Arsenic in Presence of Contaminants

Impurity	As_2O_3 Added	As_2O_3 Recovered
Mg.	*Mg.*	*Mg.*
500 Purified antimony trioxide	0.005	0.005
125 Same	0.010	0.011
125 Same	0.010	0.008
250 Same	0.020	0.020
250 Same	0.020	0.022
250 Same	0.020	0.020
250 Same	0.020	0.020
250 Same	0.040	0.038
500 Same	0.005	0.005
250 Sodium thiosulfate	0.005	0.004
250 Copper chloride	0.010	0.010
250 Lead acetate	0.010	0.010
50 Sodium hypophosphate	0.010	0.010

Arsenic was quantitatively removed without previous digestion from dilute solutions of the following organic arsenicals having arsenic in the trivalent as well as the pentavalent form:

	Av. by Gutzeit Method	Av. by Disk Method
	Mg./cc.	*Mg./cc.*
Tryparsamide	0.0025	0.0020
Neoarsphenamine	0.0012	0.0010
Tricacodylates	0.0006	0.0004
Carbasone	0.0030	0.0035
Arsphenamine	0.0010	0.0012

Acknowledgment

The author is indebted to G. S. Bohart of this laboratory for his helpful suggestions concerning this method and also to L. G. Petree for conducting many check determinations by the Gutzeit method.

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Easily Made Gas-Washing Bottle

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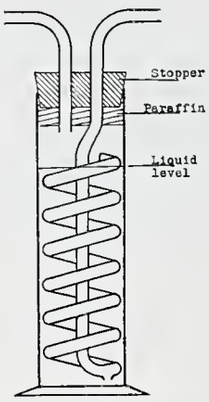

The gas-washing bottle herein described is useful because of its ease of construction and satisfactory performance. The requirements are a 5-foot (150-cm.) section of glass tubing, a glass cylinder, a rubber stopper, and a few grams of paraffin. The glass tubing is bent in the spiral form as shown so that it will fit within the glass cylinder. At the bottom of the spiral, on the under side of the tubing, a hole is blown. This is best done in a hot flame with but gentle pressure, so that the hole will not be too small. When the apparatus is assembled with the paraffin loose within the jar, the jar is inverted and heated so that the paraffin makes a gas-tight seal around the stopper and protects the latter from attack by the liquid.

In operation the gas to be washed passes down to the bottom of the central tube. As it starts up the spiral, liquid enters the tube through the hole so provided. The gas then passes up the spiral as small bubbles, acting as an air lift, the volume of the bubbles and the ratio of liquid to gas depending upon the design of the apparatus and the gas velocity. The gases remain in contact with the liquid from 10 to 40 times as long as they would if allowed to bubble unobstructed to the surface.

In the laboratory of the Philadelphia Quartz Company, this bottle of home-made construction, has, in a period of four years, been found entirely satisfactory. It has been subsequently improved first by specifying a ground-glass stopper and finally by making it of one-piece glass construction.

Received April 14, 1934.

Stainless Steel Bomb in Oxygen Calorimeter

A bomb made of stainless steel (18-8) has been in use in this laboratory for about 3 years. This bomb constitutes the essential part of an improved type of oxygen bomb calorimeter. Up to date 2593 samples of coal and 164 samples of heavy fuel oil have been burned in it. Although no linings are used, the beautiful mirror finish of its inside surface has not been dulled in the least. It appears to resist corrosion perfectly.

Fred F. Flanders

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Nature and Constitution of Shellac

VIII. Thiocyanogen Numbers of Resins

Wm. Howlett Gardner, George Pribyl, and Harold Weinberger
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This paper describes how the application of thiocyanogen may be extended to resins, and the many precautions which must be taken in preparing thiocyanogen solutions for this purpose. As a result of this investigation, new information has been obtained regarding steric hindrance and the structure of shellac.

ALTHOUGH some inorganic free radicals have been known for nearly a century, it was not until the last decade that Browne (*7*) first pointed out their similarity in properties. It was in Browne's laboratory that one of us (W. H. G.) first became interested in this field (*9*), and it was there that he recognized the analytical possibilities of free dimeric inorganic radicals. This is the first paper of a series which will describe the use of some of these new reagents in analytical work.

From their close analogy to the halogens Browne used the term "halogenoids" to described the radicals fulminate, cyanate, trinitride, thiocyanate, azidodithiocarbonate, selenocyanate, and tellurocyanate. This term describes them as a group more clearly than "pseudo-halogens," later used by Birckenbach and Kellerman (*6*). Walden and Audrieth (*36*) cite the parallel which this work bears to the now classical investigations which were carried out with organic free radicals.

Thiocyanogen

Liebig attempted to prepare free thiocyanogen (*26*) shortly after the discovery of the first halogenoid, cyanogen. A great deal of investigation followed (*11, 23, 27, 33*), but it remained for Söderbäch (*34*) actually to isolate the true free radical in 1920. This was undoubtedly because of the relative lack of stability of this compound, a property shared by some of the others and by many of their inter-halogen derivatives (*9, 12, 17, 20, 35*). In this respect they deviate most from the halogens.

Söderbäch first obtained free thiocyanogen by the action of iodine on an ethereal suspension of silver thiocyanate. He later showed that bromine gave a more complete reaction, pointing out that the solvent, the concentration, and local heat effects had an important influence on the character of the product obtained. This halogenoid may also be prepared by the oxidation of the free acid in ethereal solution with manganese dioxide, but the yield from this reaction is small (*19*). It has been prepared too by the electrolysis of thiocyanates (*21*) and by the interaction of lead tetraacetate and thiocyanic acid (*19*).

Although the tautomeric properties of thiocyanogen (*18, 36*) and its inorganic reactions are of only passing interest to the resin chemist, a number of the organic reactions studied by Kaufmann (*17*) are directly related to the chemistry of resins. With unsaturated members of the C_nH_{2n} series, thiocyanogen forms addition compounds:

$$R{-}CH{=}CHR + (SCN)_2 \longrightarrow RCH\ (SCN)\ CH(SCN)R$$

With unsaturated members of the C_nH_n series it is added only at one of the unsaturated bonds, while with compounds containing a triple bond there is no addition. Similar reactions occur with the unsaturated fatty acids. These reactions, however, are not general, since steric hindrance can prevent the addition of the halogenoid in certain cases where addition products would be expected.

Thiocyanogen substitutes in the benzene ring with aromatic amines and phenols, and one of the products is thiocyanic acid:

$$C_6H_5OH + (SCN)_2 \longrightarrow C_6H_4(OH)SCN + HSCN$$

This acid is also formed when thiocyanogen reacts with mercaptans to give disulfide compounds:

$$RSH + (SCN)_2 \longrightarrow RSSCN + HSCN$$

The first group of reactions has been used in the analysis of oils (*16*) and fats (*37*) to determine quantitatively the amounts of the different unsaturated glycerol esters. For example, in a linseed oil it is possible to calculate the exact percentage of the triglycerides of oleic and linoleic acids from the difference between the iodine and thiocyanogen numbers. Both sets of reactions offer possibilities in the analysis and study of the nature of unsaturation in resins.

Analytical Solutions

In the preparation of stable thiocyanogen solutions for analytical use, none of the authors clearly emphasize all the essential precautions, especially when it is intended to extend their use to resins.

Kaufmann (*17*) has shown that the tendency of thiocyanogen to polymerize is less in glacial acetic acid than in any other solvent. This is fortunate, since this liquid is usually one of the best solvents for resins. Kaufmann also points out that traces of moisture on the glass apparatus and exposure to the atmosphere lessen the stability. Dilute solutions (0.05 *M*) were found to give the best results. He prepared his acetic acid by treating it with phosphorus pentoxide and using the fraction distillating at 118° to 120° C. His solution of thiocyanogen was stable for more than a week and he reports that 5 hours' contact of the reagent with the oils is sufficient for complete addition.

Zeleny and Bailey (*37*), who kept their solutions in the dark, found that 17 hours were required in analyzing lard. Barbour (*3*) claims to have obtained a more stable solution by dehydrating his acid solvent with acetic anhydride. Kimura (*22*) adds the bromine during the preparation of the thiocyanogen by dissolving it in carbon tetrachloride. This modification the authors find prevents local overheating. Kimura also uses a 50 per cent excess of thiocyanogen and allows 24 hours for its reaction. Hugel and Krassilchik (*14*) recommend the use of a shaking machine during preparation of the reagent and a rapid filtration for the removal of the lead bromide formed.

Besides incorporating the best features of all these investigators, the authors found it desirable to add a 10 per cent excess of acetic anhydride to the reagent in order to remove any moisture introduced by the resin. They also proved that either chloroform or carbon tetrachloride can be used as solvent for the bromine, but that the bromine solution must

be added in very small quantities to the lead thiocyanate suspension and the mixture allowed to become completely decolorized between additions. During this operation, which takes several hours, the reaction mixture should be vigorously agitated.

The purity of the lead thiocyanate is also highly important. One of the best grades that could be purchased in the market did not give satisfactory results. For this reason in all this work, the lead thiocyanate was freshly prepared from recrystallized lead nitrate and sodium thiocyanate, and dried in a desiccator protected from light. It is essential that lead thiocyanate shall be perfectly dry in order to obtain stable solution of thiocyanogen. For the same reason a calcium chloride tube was used above the buret to protect the solution during titrations.

Method of Preparation

The methods of preparation of the reagent and the procedure found practical for resins were as follows:

Acetic Acid. Glacial acetic acid was dehydrated with phosphorus pentoxide. The supernatant liquid was then distilled in a round-bottomed flask which carried a fractionating column attached to a Liebig condenser. All connections were made with corks carefully protected with silver foil. The flask was heated in a 28° Bé. glycerol bath and the acid which distilled between 118.0° to 118.5° C. was collected and received in a suction flask which was protected from atmospheric moisture by means of a phosphorus pentoxide tube attached to the side arm.

This procedure was repeated until the product had a melting point corresponding to 99.5 per cent acetic acid, and showed no reaction with potassium permanganate when 2 ml. of the acid were diluted with 10 ml. of distilled water and 0.1 ml. of 0.1 *N* permanganate was added. As proof of this, the color did not disappear at the end of 2 hours when kept at 24° ± 3° C.

To the pure acetic acid was now added a 10 per cent excess of acetic anhydride and the solution was kept in a stoppered container protected from moisture.

Lead Thiocyanate. About 56 grams of sodium thiocyanate were dissolved in 100 ml. of distilled water, evaporated to one-half the original volume, and allowed to cool. The material which separated was filtered on a Büchner funnel and then recrystallized in a similar manner. The lead nitrate was purified in the same way.

Each salt was then dissolved in 100 ml. of distilled water and lead thiocyanate precipitated by adding the solution of the sodium salt to that containing the lead nitrate. Precipitation was carried out in the cold, since a high temperature causes decomposition of the lead haloid. The precipitated salt was then thoroughly washed with distilled water, filtered, and placed in a desiccator to dry in the dark over phosphorus pentoxide.

A determination of lead as lead sulfate on the dry material gave the following results: found, 64.15 per cent; theory, 64.10 per cent.

Bromine Solution. In 200 ml. of redistilled, water-free carbon tetrachloride 8.4 grams of pure bromine were dissolved. To this were added 300 ml. of the above specially prepared acetic acid solution.

Thiocyanogen Solution. Five milliliters of the bromine solution were then added to a suspension of 30 grams of lead thiocyanate in 300 ml. of the acetic acid, and vigorously shaken until the mixture was practically colorless before adding another portion of bromine. This procedure was followed until all the above bromine solution had been added. The mixture was then rapidly filtered through a dried, fluted filter paper. At this step if traces of moisture are present a pink color is imparted to the paper. This was avoided in all cases.

The solution was then standardized against sodium thiosulfate in the usual manner. The buret containing the thiocyanogen solution was protected from moisture with a tube containing calcium chloride or phosphorus pentoxide.

The above method gives approximately 0.1 *N* solution and retains its strength for about 8 days, as shown by the following: 15 ml. of thiocyanogen required 14.90 ml. of sodium thiosulfate solution initially; on the third day it required 14.90; on the fifth, 14.80; on the sixth, 14.75; and on the eighth, 14.75.

Procedure. Into a dry Erlenmeyer flask containing 20 ml. of the specially prepared acetic acid, 0.2000 gram of ground (30-mesh) resin was introduced, and the contents were warmed on an oil bath at 65° to 70° C. for 15 minutes to insure complete solution. Ten milliliters of pure dry chloroform or carbon tetrachloride were then added and the flask was kept at 22° ± 5° C. for 30 minutes. At the end of this time 25 ml. of the standard solution of thiocyanogen were added and allowed to react in a dark place for 48 hours.

To determine the excess thiocyanogen, 20 ml. of a 10 per cent aqueous solution of potassium iodide were added and the mixture was rapidly titrated with standard sodium thiosulfate. The thiocyanogen absorbed was calculated as centigrams of iodine in order to obtain numbers which could be readily compared with those from Wijs solution.

Thiocyanogen Numbers

Thiocyanogen numbers were determined for three unsaturated carboxylic acids, and for several samples of shellac and rosin. These numbers were compared with those obtained by using Wijs solution (*1*, *2*).

Table I. Thiocyanogen Numbers

Substance	Iodine Number	Thiocyanogen Number
Ricinoleic acid	131.8	84.6
Oleic acid (commercial)	84.3	75.2
Oleic acid (vacuum distilled)	85.6	77.7
Cinnamic acid (pure)	71.0	0.0
Methyl cinnamate	100.6	3.9
Rosin (G)	186.0	105.0
Rosin (G)	199.6	88.5
Rosin (WG)	203.1	101.7
Rosin (I)	197.3	88.4
Rosin (W. W.)	204.4	102.1
Abietic acid (commercial)	180.9	87.0
Shellac (T. N. pure)	18.0	18.4
Shellac (superfine)	19.9	19.8
Shellac (refined bleached)	9.5	9.2
Shellac (bleached)	10.6	11.1
Shellac (L & M)	19.1	18.3
Shellac (U. S. S. A. T. N.)	23.7	20.6
Shellac (U. S. S. A. T. N.)	23.0	20.0
Manila copal	69.84	44.0

As can be seen from Table I, the thiocyanogen value for ricinoleic acid is nearly that for theory, 85.03, but the iodine value is practically one and a half times that required. Ricinoleic acid, 9-octadecene-12-ol-1-acid, contains a hydroxyl group which is removed by but one carbon from the unsaturated bond. It is highly probable that with Wijs solution, the hydroxyl group in this acid is oxidized by the halogen. The literature contains no values for pure ricinoleic acid, but methyl acetyl ricinoleate has the theoretical iodine number, acetylization protecting the hydroxyl group.

The thiocyanogen number for oleic acid is lower than that required by theory, but the iodine number is also below that for a pure sample. The values are, however, the same as those obtained by other investigators (*8*, *25*) for commercial oleic acid. Vacuum distillation does not greatly increase the purity.[1]

The reaction between cinnamic acid and Wijs solution is incomplete, as shown by the very low value, while thiocyanogen is practically without reaction.

The halogenoid numbers for two grades of rosin and of commercial abietic acid are less than half the iodine number determined by the Langmuir method, but it is of interest to note that they are approximately one-half of the theoretical value, 168, for the addition of 4 atoms of halogen by pure abietic acid. It is well known that Wijs solution gives both addition and substitution with this substance (*4*, *5*, *28*, *29*, *31*). Apparently thiocyanogen adds at but one unsaturated bond and from the high degree of hydrogenation of structure of abietic acid, one would expect it to behave as a fatty acid of the $C_nH_{2n-1}O_2$ series.

The two numbers are practically identical for pure shellac. The differences for the U. S. Shellac Association T.N. grades is due entirely to the presence of rosin as shown by calculating the percentage of rosin both by the Langmuir formula (*2*) and by the difference in the two absorption numbers. The results agree within 0.2–0.3 per cent. It would appear, there-

[1] In the discussion of this paper at Washington, J. S. Long stated that he had obtained similar results, but that when the acid was purified by the method of Lapworth, Pearson, and Mottran, *Biochem. J.*, **19**, 7 (1925), both the thiocyanogen and iodine values correspond to theory.

fore, that there is some theoretical chemical basis for the results obtained by the Langmuir method (*24*). For this reason the Langmuir values should not be treated as purely empirical, when considering them in connection with those of other methods, such as the Hübl method.

The iodine number for the superfine shellac is abnormal for this grade. This sample contained 0.45 per cent of arsenious sulfide, and Rangaswami and Aldis (*32*) have shown that if this adulterant is in a finely divided state, it will increase the iodine number. Apparently it affects both thiocyanogen and iodine numbers equally.

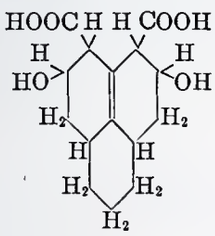
Steric Hindrance

These results bring to light certain other theoretical considerations, such as the effect of steric hindrance (*15*) which investigators are apt to overlook. The authors' values for cinnamic acid present a typical case. It is well known that while chlorine and bromine add quantitatively to this acid, the absorption of pure iodine is very slow. This is caused by the proximity of two strongly negative groups, phenyl and carboxyl, to the unsaturated bond of the acid. In view of these facts, it was not surprising to find that the less reactive thiocyanogen gave no reaction.

If the authors' theory is correct, values for methyl cinnamate should be better than those for the free acid, since the methyl group should decrease the negative character of the carboxyl group. As can be seen from Table I, this is true for the addition of iodine, but the negative groups still prevent the addition of thiocyanogen.

This would explain the behavior of this halogenoid with fatty acids of the $C_nH_{2n-1}O_2$ series where the addition of one molecule of thiocyanogen would prevent the absorption at the second, and hence, as is observed, the thiocyanogen number is one-half of the iodine number.

The consideration of steric hindrance is also of interest from the point of view of postulation of the constitution of shellac, since Harries and Nagel have found that the only isolated unsaturated acid (*10, 13, 30, 31*), shellolic acid, did not absorb bromine (*13*). To account for this they have postulated an internal unsaturated bond in its structure:



The question, then, naturally arises as to why shellac should have an iodine number. It can be readily demonstrated by acetylization that Wijs solution does not replace hydroxyl groups in this resin, so that some other explanation is necessary.

The facts as they are known can be readily explained if cinnamic acid and methyl cinnamate are used for analogy. If we assume that the double bond in shellolic acid is adjacent or close to the carboxyl groups, it is easy to understand why halogens may not be absorbed by the free acid, but if in the structure of shellac these same carboxyl groups form part of the ester linkages, it would be clear why the resin itself showed unsaturation. The large molecules, attached to these acid groups of shellolic acid, should have a marked effect in decreasing their negative character, so that a thiocyanogen number for shellac would not be considered unreasonable.

Conclusions

Halogenoid solutions may be used to give the chemist another method by which to study the nature of unsaturation and the constitution of resins. Because of the difference between the iodine and thiocyanogen numbers of different resins, it may be possible to develop methods for the quantitative determination of some of these resins in varnish mixtures.

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Detection and Determination of Solvents and Volatile Liquids in Nitrocellulose Lacquers and Lacquer Thinners

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WITHIN the last few years, various new solvents for use in the lacquer industry have made their appearance on the market. Some of these solvents are sold under trade names which afford no certain clue to their actual chemical identity; or they may be encountered as unknown components of finished nitrocellulose lacquers or of the thinners sold with such lacquers.

For the purpose of appraising a solvent, thinner, or lacquer as to probable value and behavior on application or in use, it is often highly desirable to know the identity of the liquid or liquids it contains, as well as the approximate composition of the mixture in case a thinner or lacquer is involved. For this purpose a practical method for the quantitative determination of low-boiling and high-boiling solvents and diluents, followed by their identification, is here presented.

Solvents are distilled from the lacquer at atmospheric pressure, low-boiling partly water-soluble components being taken off first, followed by removal of higher-boiling components after the addition of water. Distillation under reduced pressure may be desirable for the removal of super-high-boiling compounds, but in general is not recommended since it entails the possible loss of volatile components.

Lacquers formulated with the esters of lactic acid require a special procedure which will not be described in this paper.

Quantitative results are obtained by analysis of two fractions—the fraction boiling up to 93° C. and the fraction boiling above 93° C. Components are identified by fractional distillation of the products of alkaline saponification. Identification tests for the more commonly used lacquer solvents and diluents are described. Results obtained by the method described have been found to agree closely with the actual composition of known lacquers and thinners.

Quantitative Determination of Esters, Alcohols, and Total Hydrocarbons

Analysis of Thinner. Two hundred and fifty cubic centimeters of thinner are slowly distilled through a good fractionating column until a vapor temperature of 93° C. is reached. At 93° C. all ethyl compounds will have been distilled over. If iso- or secondary butyl compounds are present, small amounts of these compounds may come over with ethyl acetate below 93° C. The volume of distillate is measured and recorded; and esters, hydrocarbons, and alcohols on both distillate and residue are determined as follows:

Esters are determined on both the distillate and the residue by saponifying 2 cc. of sample with 25 cc. of 1 N alcoholic sodium hydroxide. The mixture is refluxed for 1.5 hours, and the excess sodium hydroxide titrated against standard acid. Saponifiable matter in the distillate is calculated as ethyl acetate and converted from grams per 100 cc. to per cent by volume of 88 per cent commercial ethyl acetate by dividing by (0.9 × 0.88). Esters in the residue above 93° C. are calculated as butyl acetate and converted from grams per 100 cc. to per cent by volume of 92 per cent commercial butyl acetate by dividing by (0.88 × 0.92).

Hydrocarbons are determined on both the distillate and the residue by mixing 20 cc. of sample with 20 cc. of 80 per cent sulfuric acid (80 cc. of concentrated sulfuric acid plus 20 cc. of distilled water) in a 50-cc. buret which has been sealed off at the lower end. After thorough shaking, the mixture is allowed to stand overnight in an upright position, and the percentage by volume of hydrocarbons is calculated from the volume of the upper layer. Erroneous results will be obtained if the strength of the sulfuric acid deviates more than ±3 per cent from the 80 per cent specified.

Alcohols are determined on both the distillate and the residue by mixing 50 cc. of sample with 200 cc. of water in a 250-cc. graduated cylinder. The percentage of alcohols is determined by decrease in volume of upper layer from the original 50 cc. This determination is approximate only, and is used as a check. In final calculations, alcohols are estimated by difference.

In case the volume of either distillate or residue is insufficient for the determination of alcohols, as outlined above, 10 or 20 cc. of sample may be mixed with an equal volume of distilled water in a 50-cc. buret sealed at one end. If the sample is insufficient for esters, hydrocarbons, and alcohols, determination of the alcohols should be omitted or a larger amount of sample taken for fractional distillation at the start. Alcohols as determined on the distillate below 93° C. should be fairly accurate, but results on the residual portion (above 93° C.) will be somewhat low and merely indicative of the presence or absence of free higher alcohols.

If time is available, a valuable check may be obtained on the values derived above by determining esters, hydrocarbons, and alcohols on the sample as received, following the procedure outlined above. In this case, esters calculated as butyl acetate will be higher than actual, the error being in proportion to the ratio of butyl acetate and ethyl acetate present in the thinner. Very little extra time is required to make these determinations if run simultaneously with tests outlined above.

Table I. Typical Analysis of Sample of Thinner

	Hydrocarbons	Esters	Alcohols
	%	%	%
As received (by volume)	55.5	28.58	16.0
HIGH- AND LOW-BOILING FRACTIONS (250 CC. DISTILLED)			
Below 93° C. (80 cc., 32% by volume)	47.75	21.32	42
Above 93° C. (170 cc., 68% by volume)	58.75	29.64	12
CONVERTED TO PERCENTAGES OF ORIGINAL THINNER			
Low-boiling	15.28	6.82	13.44
High-boiling	39.95	20.16	8.16
	55.23	26.98	21.60
	26.98		
	21.60		
	103.81		
ALCOHOLS CALCULATED BY DIFFERENCE			
Low-boiling	15.28	6.82	9.90
High-boiling	39.95	20.16	7.89
	55.23	26.98	17.79

Calculating the alcohols by difference is believed to be more accurate, in that it allows for the alcohols which normally are present in the commercial acetates. This analysis agrees fairly closely with results for the material as received, and indicates the following approximate formula, subject to confirmation and identification later:

	%
Hydrocarbons	55.0
Ethyl alcohol	10.0
Ethyl acetate	7.5
High-boiling alcohols	7.5
High-boiling esters	20.0
	100.0

Analysis of Lacquer. After separation of the total volatile constituents from the solids, analysis of a lacquer is identical with that of a thinner, except that the amount of sample available is less, and that it may be advisable, from the point of view of the extra time involved, to omit determinations on sample as received and confine the analysis to examination of low- and high-boiling portions.

For unthinned lacquers of average viscosity, 1030 cc. are poured into a graduated cylinder (the 30-cc. mark is estimated on a 1000-cc. cylinder) and transferred to a 3-liter round-bottomed flask. In this way allowance is made for the lacquer which adheres to the sides of the cylinder and the actual sample taken is 1000 cc. The flask is fitted with two thermometers, one reaching into the lacquer and one to record the vapor temperature in the neck of the flask. The flask is immersed in an oil bath in which a third thermometer is immersed. To avoid the difficult operation of drying the low-boiling alcohols and esters, distillation is conducted slowly and carefully on the water-free lacquer until a vapor temperature of 93° C. has been reached. At this point a cut is made, and, if the lacquer still appears to be fairly liquid, distillation is continued and as much high-boiling (from 93° C. upwards) liquids as possible recovered before stopping the distillation and adding water. However, caution is advised at this point and the temperature of both the oil bath and the liquid lacquer should be carefully watched, so that the oil bath does not go above 150° to 155° C. and the liquid lacquer above 110° C.

When the liquid lacquer temperature has reached 110° C., distillation is discontinued and, as soon as the apparatus is cool enough for handling, 500 cc. of distilled water are added and heat again applied. Distillation is continued until about 1100 cc. of total distillate, dry and aqueous, have been collected. The distillate towards the end should be tested for the presence of solvents by tasting and by collecting a small portion and treating with anhydrous potassium carbonate. In some cases a second portion of 300 cc. of distilled water may be necessary for complete removal of solvents.

When tests show that the solvents have all been extracted, the aqueous distillate, including small amounts used for testing, is dried with potassium carbonate and added to any nonaqueous distillate collected above 93° C. Drying of the high-boiling liquids is much easier and more complete than when low-boiling distillates are present. Determination of alcohols, esters, and hydrocarbons is then made according to the procedure outlined for analysis of thinner. If desirable and time permits, the dried high-boiling liquids can at this point be mixed with the low-boiling portion, and total esters, hydrocarbons, and alcohols determined. However, if this be done, it is desirable to refractionate the mixture up to 93° C., since identification of the low-boiling solvents, assumed to be ethyl alcohol and ethyl acetate, is usually omitted, and identification of the high-boiling solvents is more positive in the absence of the ethyl compounds.

Identification of Volatile Constituents

In the identification of the volatile constituents of a lacquer or thinner, close attention should be paid to distillation temperatures, as much can be learned in this way. Low-boiling naphtha may be detected by initial boiling point, or, in the rare cases in which it is used, acetone may be detected by its boiling point and otherwise confirmed later. The absence of saponifiable matter discovered in the foregoing scheme of analysis would indicate a solvent of the cellosolve type. Cellosolve may be readily identified by its boiling point, water solubility, solvent action on nitrocellulose, and odor after separation from hydrocarbons in the manner to be described. Its approximate percentage by volume may be determined by fractional distillation of the nonhydrocarbon material.

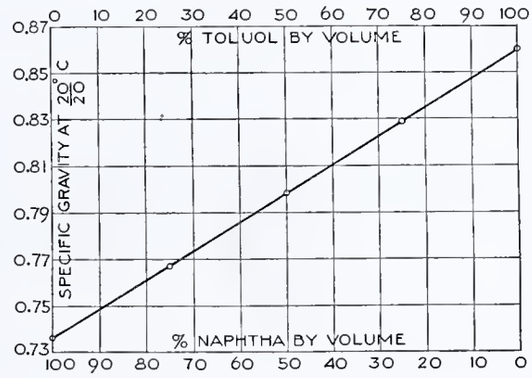

Figure 1

For identification of the solvents and diluents in a standard lacquer or thinner of the alcoholic ester type, 500 or 1000 cc. (depending on the amount of hydrocarbons present) of sample are thoroughly mixed with an equal volume of cold sulfuric acid (80 cc. of concentrated sulfuric acid plus 20 cc. of distilled water). The mixture should be kept cool during mixing to prevent losses by evaporation, or to minimize decomposition due to heating. In some cases the use of 85 per cent phosphoric acid rather than 80 per cent sulfuric acid may be found preferable, but in general the much higher cost of phosphoric acid will make its use in large quantities undesirable. For the quantitative estimation of hydrocarbons in the analysis of lacquers and thinners, cold sulfuric acid has been found to give more accurate results than 85 per cent phosphoric.

In the analysis of a lacquer, if the quantitative determinations and the distillations preceding it tend to show that the low-boiling solvents are ethyl compounds, further treatment of this portion is unnecessary, unless identification of the possible low-boiling hydrocarbons is important. The entire high-boiling portion left after quantitative determinations of hydrocarbons, esters, and alcohols is treated with an equal volume of 80 per cent sulfuric acid. The solvent hydrocarbon–sulfuric acid mixture is allowed to settle in a separatory funnel, and the lower layer of alcohols and esters in sulfuric acid is drawn off. The upper hydrocarbon layer is examined for composition and the presence of naphthas, toluene, and

Table II. Properties of Alcohols Present in Indicated Esters

Ester	Boiling Range or Point ° C.	Refractive Index	$ZnCl_2$–HCl Test	Iodoform Test
n-Butyl acetate	117.7	1.3993	Perfectly clear solution. No upper layer on standing	Negative
Secondary butyl acetate	90–101	1.397	Deep upper layer	Positive in one minute
Fermentation amyl acetate	78–130.5	1.361 to 1.406. Principal fraction from 120° to 130.5° C. is 1.406	No upper layer in any fraction	None in amyl alcohol range. Trace in low-boiling fraction
Amyl acetate from unsaturated hydrocarbons	110–135	Mixture of alcohols is 1.4078. Principal fraction 117° to 119° C. is 1.406. Last fraction 134° to 135° C. is 1.413.	Upper layer in all fractions	Positive test in 5 minutes or less in all fractions
Amyl acetate from saturated hydrocarbons	117–137	1.404 to 1.410. Principal fraction boiling from 120° to 136° C. is 1.410	Upper layer in first fractions fading out above 130° C.	Positive test in fractions below 120° C. Heavy precipitate in 117° to 120° C. fraction. Trace only above 120° C.
Higher alcohols acetate by catalysis, mostly isobutyl acetate	105–130	1.388 to 1.420. Principal fraction boiling from 106° to 112° C. is 1.396	Upper layer in last fraction only	Negative in all fractions

xylene determined by correlation of boiling ranges and specific gravities of naphtha, and toluene and xylene, so that it is easy to detect the presence of the former in admixture with the two latter compounds. Figure 1 gives the specific gravities of mixtures of lacquer diluent naphtha and toluene.

However, in cases where it is important that the actual composition of the hydrocarbons be known, the following method will give very close approximations:

Fifty cubic centimeters of the mixed hydrocarbons are measured into a 500-cc. Erlenmeyer flask. To the flask are added 100 cc. of approximately 100 per cent sulfuric acid made by adding 50 cc. of reagent fuming sulfuric acid containing 20 per cent excess of sulfur trioxide to 50 cc. of reagent sulfuric acid (1.835 specific gravity). This mixture is stoppered and thoroughly shaken at least three times during a 15-minute reaction period. The contents are then poured into a 250-cc. glass-stoppered graduated cylinder and after 1 hour the percentage of petroleum hydrocarbons is calculated from the volume of the upper layer, the coal-tar hydrocarbons having been completely sulfonated.

The presence of xylene may be detected by nitrating the hydrocarbon mixture in two parts of sulfuric and one part of nitric acid. The crystalline nitration products are separated from the excess acid, washed in water, and dried at 60° C. Trinitrotoluene is soluble in ethyl alcohol and melts at 78° to 80° C.; trinitroxylene is insoluble in alcohol and melts at 180° to 182° C.

The sulfuric acid solution of the alcohols and esters is slowly diluted with at least three times its volume of distilled water, precautions being taken to avoid heating the mixture at the start of the dilution. Through a short fractionating column the alcohols and esters are distilled off with water, and the water is removed by salting out with potassium carbonate. The dried mixture may be analyzed for ester and alcohol content by the method given for analysis of thinner, or, if the volume is not large enough, 2 cc. may be taken for ester determination and the alcohols estimated by difference. If these data are desired, it will be necessary to redistill the dried solvents to remove any dissolved potassium carbonate, as this would interfere with the determination of esters by alkaline saponification.

The dried alcohols and esters are now saponified in the following way:

Crushed sodium hydroxide sticks or pellets, equal in weight to one-third of the weight of the alcohols and esters, are dissolved in an equivalent number of cubic centimeters of distilled water with constant stirring to take advantage of the heat generated. After complete solution the liquid is cooled, and a volume of methanol equal to twice the amount of water used is added. This alkaline solution is now added cautiously to the alcohol-ester mixture in a suitable size round-bottomed flask. The mixture is refluxed for 0.5 hour under a good fractionating column, after which the known amount of methanol is distilled off and discarded. The alcohols are then distilled off and the wet fractions dried with potassium carbonate.

Several refractionations may be necessary to divide the alcoholic mixture into its true fractions. At this point, much will be known of the probable identity of the alcohol or alcohols, and 5- to 10-cc. cuts of the apparently pure fraction should be made, using the theoretical boiling point of the suspected alcohol as a guide. These small pure fractions can be used for identification tests, such as refractive index and the zinc chloride–hydrochloric acid test for characterization as primary, secondary, or tertiary alcohol.

The alcohols from the original esters, as well as any high-boiling free alcohols originally present, are now ready for identification, and the following data should be obtained:

1. Volume–per cent distribution of the different fractions present, for use in comparison with the same values for known alcohols or mixtures of alcohols used in the lacquer industry.
2. Refractive indices of all fractions.
3. The zinc chloride–hydrochloric acid test on all fractions for characterization as primary, secondary, or tertiary alcohols. This test, described by Lucas (*1*), has been found very satisfactory in distinguishing between the more commonly used primary and secondary alcohols. The reagent for this test is made by dissolving 136 grams (1 mole) of anhydrous zinc chloride in 105 grams (1 mole) of concentrated hydrochloric acid with cooling. The test is carried out by adding 2 cc. of the alcohol in a vial or test tube to 12 cc. of the zinc chloride–hydrochloric acid reagent, stoppering with a cork, and shaking. Alcohols lower than hexyl are soluble in this amount of the reagent, but tertiary alcohols react so fast that separation of tertiary chloride as an upper layer is noticeable almost at once. If a secondary alcohol is present, the clear solution becomes cloudy in about 5 minutes and, on standing overnight, a distinct upper layer is visible. In the case of a primary alcohol, no change, except a slight darkening, takes place even on long standing. By the use of larger amounts of alcohol and reagent in standard test tubes, such as Nesslers, the method may be made more or less quantitative for mixtures of secondary and primary alcohols by measuring the upper layer formed and comparing its volume with the volume of chloride produced by a known alcohol or mixtures of alcohols.
4. In case positive tests for secondary alcohols are obtained in 3, the iodoform test for secondary alcohols should be made. In addition to isopropyl, which is little used in the lacquer industry, both secondary butyl and secondary amyl alcohols have been found to react with iodine at room temperature in alkaline solution. Two or three drops of the alcohol are dissolved in 10 cc. of 1 *N* sodium hydroxide solution, and 15 or 20 cc. of 0.1 *N* iodine are run with constant shaking. A yellowish white precipitate of iodoform, visible in a minute in the case of the secondary amyls, indicates these alcohols.

Correlation of Data. With the above data at hand, the nature or source of the alcohols present originally, mostly as esters, may be fairly accurately determined by a process involving elimination and comparison. The esters most commonly used in the lacquer industry are ethyl acetate, secondary butyl acetate, normal butyl acetate, amyl acetate (from fusel oil), secondary amyl acetate by synthesis from unsaturated hydrocarbons, amyl acetate by chlorination of saturated hydrocarbons, and the acetates of synthetic alcohols by catalysis from hydrogen and carbon monoxide (mostly isobutyl alcohol). Cellosolve and its esters will be recognized by special tests referred to above.

Ethyl acetate is universally used in lacquer formulas, is easily separated from the higher-boiling compounds, and its presence as the low-boiling ester is generally assumed in lacquer analysis, unless contradictory behavior of some sort is noticed, in which case identification could be made by well-known methods. The characteristics of the six other types can be summarized as in Table II.

From these data it is possible to recognize with certainty any of the esters of the foregoing list present in a lacquer or thinner. For example, *n*-butyl compounds can be readily identified by the narrow boiling range, the refractive index, the absence of any upper layer in the zinc chloride–hydrochloric acid test, and the negative test for iodoform. Further confirmation may be obtained by determining the melting point of the dinitrobenzoate (*2*, *3*). Secondary butyl alcohol may be identified by its boiling point, its very positive reaction in the zinc chloride–hydrochloric acid and the iodoform tests, and by its characteristic odor. Fermentation amyl alcohol is distinguished by its boiling range and the negative test with zinc chloride–hydrochloric acid in all fractions. Amyl alcohol from unsaturated hydrocarbons is identified by its characteristic odor, and the positive reaction of all its fractions in the zinc chloride–hydrochloric acid and the iodoform tests. This commercial product is made up largely of secondary alcohols in contrast to the amyl alcohols from saturated hydrocarbons, which are largely primary amyl alcohols, and have a higher average boiling point. The latter compounds may be distinguished from fermentation amyl alcohols by the presence of the lower-boiling secondary compounds. The higher alcohols produced from hydrogen and carbon monoxide may be identified by the high isobutyl alcohol content and the negative iodoform test in all fractions.

For more positive identification when necessary, the melting point of the 3,5-dinitrobenzoic acid derivative, referred to above, may be found helpful.

The following method devised by the author has been found to give closely approximate results for the determination of secondary butyl compounds in mixture with normal butyl compounds:

Ten cubic centimeters of thinner, or 10 cc. of the total volatile matter from a lacquer, are carefully weighed into 50 cc. of 1 *N* aqueous potassium hydroxide solution in a stoppered flask. Refluxing for 3 to 4 hours with frequent shaking, using a long condenser, has been found to yield practically complete saponification of the esters. The saponified mixture is then titrated to neutrality with 0.25 *N* sulfuric acid solution, and the esters are calculated as a check on previous quantitative determination. The neutral solution is diluted with about 100 cc. of distilled water, and the alcohols are distilled off in about 75 cc. of water. The distillate is made up to 150 cc., thoroughly mixed, and a 25-cc. aliquot pipetted into a 500-cc. flask containing 100 cc. of sulfuric acid (1.35 specific gravity). Fifty cubic centimeters of 1 *N* potassium dichromate are now run in slowly from a buret with constant shaking and maintenance of the temperature at 10° to 15° C. The mixture is allowed to stand for 30 minutes after the last of the bichromate has been added. It is then diluted to 600 cc. and distilled, 250 cc. of distillate being collected in a flask immersed in a bath of water at 15° C. The 250 cc. of distillate are thoroughly mixed, and a 25-cc. aliquot is pipetted out for determination of methyl ethyl ketone by the Messenger method, as follows:

Fifty cubic centimeters of 1 *N* potassium hydroxide are measured from a cylinder into a 750-cc. Erlenmeyer flask. The 25-cc. aliquot from the 250 cc. of distillate is added, and 50 cc. of 0.1 *N* iodine are added from a buret with constant shaking. The mixture is allowed to stand at room temperature for about 20 minutes, after which the excess iodine is titrated with 0.05 *N* sodium thiosulfate using starch as the indicator. A blank must be run on the reagents, omitting the sample.

The approximate percentage of secondary butyl acetate by weight is calculated as follows:

$$\frac{(\text{cc. of thiosulfate for blank} - \text{cc. of thiosulfate for sample}) \times \text{normality of thiosulfate} \times 60 \times 0.01935 \times 100}{\text{weight of sample (10 cc.)}} = \%\ \text{secondary butyl acetate}$$

For the detection of other mixtures of the six typical groups of solvents discussed in this article, considerable ingenuity may be necessary, but a reliable opinion may be formed by comparison of the suggested properties, the volume-per cent distribution of the different alcohols as to boiling temperature being especially helpful in detecting mixtures or adulterations.

Literature Cited

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Determining Flex Cracking in Treads

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A method for comparing the flex cracking properties of tread stocks on standard tires which permits the use of laboratory-mixed batches is presented. The method can be adapted to the testing of the effect of carcass construction, tread design, etc., on flex cracking. Comparative tests on tires of different make can also be made. Laboratory results check with information obtained from the road.

THE initiation and growth of cracks are obviously important factors in the service rendered by tire treads. Several machines have been designed to give comparative data on the flex resistance of various compounds, but in the experience of the present authors, none of the available methods for flex cracking comparisons are satisfactory, since predictions based upon them are not confirmed by road tests. As a result, a great deal of time and money has been wasted in developing compounds in the laboratory only to meet with failure on the road.

Any new method should permit a fairly accurate means of estimating the tendency towards initiation of cracks and a quantitative measure of cracks and cuts once formed. In addition, it should be adapted to studying the effect on cracking of various compounding ingredients such as age resisters, of varying such physical properties as modulus, hardness, etc., of cure, methods of mixing, tread design, tread contour, etc. The method should also permit the use of either laboratory- or factory-mixed stock. Before the present work was completed, it was found possible to make fairly accurate studies of various construction details of the tire carcass on tread cracking as well as to compare the products of various manufacturers.

Definite knowledge on formation of cracks due to flexing is necessary. On the other hand, in many types of service, tires are subjected to the action of sharp objects, such as cracked stones, which will cut the tread. Such cuts are not always harmful. If there is a tendency to grow, however, the cut will, in time, extend to the carcass and serious trouble result. Some tread designs will pick up stones, which may cut the undertread before they are expelled. Here again, in many cases, if the cuts do not grow to any extent, very little harm is done.

Description of Test

Obviously, the only way to test a tread that would answer all the above qualifications would be on a tire. A 7.00-18, 6-ply tire was used exclusively for the preliminary work on laboratory-mixed batches. Other sizes varying from a 5.25-18, 4-ply, to a 10.50-22, 12-ply, have been satisfactorily used.

One standard and three experimental sections can be tested on a single tire. The raw materials for the four batches, except the particular items to be tested, are always taken from the same lot. If possible, the major portion of the batches are mixed in a master batch in the factory. The batches, generally 10 pounds, are mixed on a 24-inch laboratory mill. The stock is sheeted off about 0.125 inch thick, and while still warm is cut and plied up to approximate the shape of the mold described in the next paragraph. Care must be taken not to trap air between the plies.

The plied-up stock is now ready to be molded. The mold used is merely a flat plate, machined out to a cavity which in cross section equals the contour and gage of a tubed 7.00 tread. The length of the cavity is about 3 inches greater than one-fourth that of a 7.00-18 tread. A standard sheet-metal cover is used. The

Table I. Variation in Aging Period[a]

Days in Aging Oven	Crack Growth Index	Number of Flex Cracks
None	100	0
2	144	0
5	268	39
7	330	71
9	403	109
21	830	186

[a] Both crack growth index and number of independently formed flex cracks vary with the increase in time in the aging oven.

Table II. Limits of Test

Part 1. Variation in Length of Cracks in a Given Section[a]

	Length of Cracks in Inches[b] Gr. 1	Gr. 2	Gr. 3	Gr. 4	Average Crack Growth %	Crack Growth Index	Number of Flex Cracks
Unaged compound							
A	0.37	0.43	0.40	0.36			
	0.39	0.41	0.38	0.42			
	0.46	0.41	0.41	0.41			
Av.	0.41	0.42	0.40	0.40			
% increase	64	68	60	60	63	100	None
B	0.35	0.35	0.35	0.38			
	0.35	0.36	0.33	0.34			
	0.35	0.33	0.34	0.33			
Av.	0.35	0.35	0.34	0.35			
% increase	40	40	36	40	39	62	None
Aged compound							
A	0.72	0.83	0.75	1.02			
	0.90	0.88	0.74	1.06			
	1.03	0.81	0.81	0.98			
Av.	0.88	0.84	0.77	1.02			
% increase	252	236	208	308	251	100	107 (large)
B	0.70	0.69	0.64	0.81			
	0.80	0.74	0.65	0.76			
	0.73	0.54	0.56	0.65			
Av.	0.74	0.66	0.62	0.74			
% increase	196	164	148	196	176	70	61 (small)

Part 2. Variation from Tire to Tire

Test no.	Crack growth index[c] Unaged	Aged
1	68	84
2	76	75
3	83	..
4	86	80
5	89	96
6	65	83
Av.	78	83

[a] Of two sections, the one with the larger average growth will generally show the greater variation from cut to cut within the section. Three cuts were placed in each of four grooves.
[b] Original length of each crack, 0.25 inch.
[c] On basis of standard as 100.

Actual percentage growth of both compounds on some tires was considerably greater than on others, but variation of crack growth index of the experimental on the basis of the standard as 100 is not extreme.

Table III. Comparison of Growth of Cracks in Molded and Extruded Treads from Same Batch[a]

Compound	Unaged Molded %	Unaged Extruded %	Aged Molded %	Aged Extruded %
R	51	52	276	272
S	53	55	245	240

[a] Variation shown is no greater than would be expected from two halves of a tire with a single tread.

Table IV. Accelerator Comparisons[a]

Accelerator	Bureau of Standards Machine: Unaged Crack growth index	Unaged No. of flex cracks	Hot room Crack growth index	Hot room No. of flex cracks	Aged Crack growth index	Aged No. of flex cracks	Road Data Crack growth index
A	100	0	100	1	100	186 large	100
E	53	0	68	0	23	5 very small	67
F	41	0	...	.	...	...	62
B	40	0	36	0	24	97 very small	56
G	39	0	...	.	...	...	47

[a] All stocks were cured to optimum conditions as judged by cure analysis.

Table V. Age Resister Comparisons

Age Resister[a]	Bureau of Standards Machine: Unaged Crack growth index	Hot room Crack growth index	Aged Crack growth index	Aged No. of flex cracks	Road Data Crack growth index
A	100	100	100	90 large	100
C	93	..	86	66 large	98
B	81	..	60	74 small	90
D	76	82	72	26 small	89
E	78	78	83	32 small	79
F	77	62	70	66 very small	76
G	133	134	148	67 large	..

Amount of Age Resister on 100 Rubber[b]	Aged Crack growth index
0.75	100
1.00	72
1.50	36

[a] Small amount of age resister.
[b] Increasing amount of age resister. Choice of age resister as well as amount used is of extreme importance in development of a tread stock.

Table VI. Comparison of Carbon Blacks from Various Sources[a]

Black	Bureau of Standards Machine Crack growth index aged	Road Data Crack growth index
B	82	80
C	79	88
D	102	97
A	100	100
F	116	113
E	104	116

[a] All batches were mixed in the factory under standardized conditions. The blacks were equally well dispersed. The laboratory data place the black in the same order as the road except that E and F are reversed.

mold and cover are heated in a press to approximately the temperature of the stock as it comes from the mill.

A sheet of parchment paper is placed on each side of the built-up tread slab. The slab is then placed in position in the mold, and the mold placed in a press and cooled under pressure.

The standard and three experimental sections are cut to one-fourth the length of a 7.00-18 tread. The sections are spliced to form a full tread, built into a tire, cured, and are ready for test.

As samples from factory-mixed batches can be used as well as laboratory batches, all desired variations in factory processing can be studied. By using laboratory-mixed batches, it is possible to obtain information on materials available only in small quantities. The use of both factory- and laboratory-mixed batches permits the study of all available materials. Factory-mixed experimentals are checked against factory-mixed standard and laboratory-mixed experimentals against laboratory-mixed standard.

Molded treads have been checked against extruded treads and found to be equal in resistance to cracking. In testing this point, the stock in a given test was from the same factory batch. Part of the batch was held out for the preparation of two molded sections and the rest extruded in the regular way. These two molded sections were spliced to make half a tread. The other half was taken from the extruded ribbon. Crack growth on the extruded and molded tread from the same batch was identical.

After the tire has been cured, a series of 12 cuts is made with a special tool in the tread design in each of the stocks at definite points, relative to the design. The blade of the knife is approximately 0.031 inch thick and is exactly 0.25 inch long. The knife is fitted with a shoulder so that the blade cannot penetrate the surface more than 0.016 inch. The cut formed is 0.25 inch long by 0.016 inch deep. After the tire has been run, the length of the cuts is measured. The increase over 0.25 inch multiplied by four gives the percentage increase. The average increase of the 12 cuts in a given section is used on the crack growth percentage for the section.

After the cuts have been made, the tire is mounted and inflated as desired, generally using loads and inflations recommended by the Tire and Rim Association. The tire is then run on a Bureau of Standards test wheel at 45 miles per hour 2000 miles at room temperature, the tire is removed, and the increase in length of the cuts is recorded. Examination may reveal independently formed flex cracks with some tread compounds.

In the first part of the work on this problem, the tires, after the original 2000 miles, were replaced on the machine, using the same

Table VII. Tests Run on 9.75-22 Tires

	Bureau of Standards Machine				
	Unaged		Hot room		
Compound	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks	Road Data[a]
C[b]	100	36	100	Very numerous (not counted)	Cracked badly
D	43	7	31	36	No cracking

[a] Results from tires in service in various parts of the country. Half-and-half tread tires.
[b] It was necessary to remove some of the tires from service because of excessive cracking in section C.

Table VIII. Flex-Cracking Comparison of Age Resisters on Bureau of Standards Machine and on Crushed Stone Roads[a]

			Stone Road			
			Unaged		Aged	
Age Resister	Bureau of Standards Machine Unaged	Bureau of Standards Machine Aged	In grooves	Radial in side-wall	In grooves	Radial in side-wall
M	1	90 large	14	3	70	69
N	9	66 v. small	5	1	31	5

[a] Average number of flex cracks of four tires on both road and Bureau of Standards machine. The tires were run 6000 miles.

Table IX. Effect of Cure Variation[a]

	Unaged		Aged	
Cure	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks
A (optimum cure)	100	0	100	290
B (over-cure)	114	0	122	475

[a] Corresponding road data are not available.

Table X. Tread Design Comparison

	Bureau of Standards Machine Crack Growth Index		Road Data
Tread Design	Unaged	Aged	Crack Growth Index
A	100	100	100
B	40	62	77
C	88	79	[a]
D	100	100	[a]
E	102	136	[a]
F	126	92	[a]
G	149	164	[a]

[a] Crack growth index relationship of the aged tires not the same as on the unaged tires. Facilities did not permit testing on the road.

initial load and inflation, and were run an additional 1500 miles. In this second phase, however, the temperature of the room was maintained at 46° C. (115° F.). Crack growth percentage and number of independent flex cracks were again recorded.

As the work progressed, it was found that the test was not drastic enough and it became necessary to develop an aging procedure. The tires, after running the initial 2000 miles, are removed from the rim and hung on a truck which is placed in an oven maintained at 82° C. (180° F.). The tires are left in the oven for 16 hours and are then removed for 8 hours. This cycle is repeated seven times. It is felt that the alternate heating and cooling is more nearly like natural aging than continued heating would be. The tires are then run for 1500 miles at room temperature as described above. This modified test brings out enormous differences between various stocks both in growth of cracks and flex cracks. However, some tires are still tested in the hot room as a check.

The method has been checked by hundreds of tests in the field. In the field tests, half tread tires were built. Tests were run on the test cars, mileage accounts, and the regular commercial accounts, and in various sections of the United States. Without exception, stocks that show low crack growth, and few if any flex cracks after the aging period, will perform better on the road as far as cracking is concerned than those that show a larger number of cracks and greater crack growth on the indoor test.

A still further check on the laboratory procedure is to age tires with half-and-half treads for 7 days, as described, without previously running them on the wheel. If such tires are then run on a gravel or crushed stone road, the cracking tendencies will check the results obtained on the indoor machine although percentage relationship will vary. Furthermore, such tires have all the appearance of having been run for a season or so in a region where crushed stone roads predominate.

Table XI. Varied Thickness of Undertread[a]

	Unaged		Aged	
Undertread	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks
Thick	100	0	100	77
Thin	178	0	183	245

[a] Comparison given merely to show how much cracking can be varied using same compound.

Table XII. Effect of Dirt and Grit on Tread Cracking

	Number of Flex Cracks	
Tread	Unaged	Hot room
X	7	10
Y[a]	Very numerous (not counted)	Very numerous (not counted)

[a] Three per cent of grit from black and dirt from various places in the factory added to tread Y. Test used as example in a campaign against dirt.

For the most part, it is unnecessary to run more than one tire where the standard stock is on the same tire as the experimentals. Where comparisons are to be made from tire to tire, however, it is always advisable to run parallel tests.

Experimental Data

In Tables I to XII, the basic compounds are the same in any given table although the compounds are not the same from table to table. Percentage relationships from comparisons run on the road and in the laboratory are not exact but for the most part are close approximations and are almost invariably in the same direction.

Comparisons of increase in length of the cuts are carried under the heading "Crack Growth Index." In all cases, the growth of the cuts in the standard section or tire is considered as 100. Values less than 100 mean that the cracks grew less than the standard, while those larger than 100 indicate greater growth. The number of independent cracks formed is listed under "Flex Cracks." In most cases, the approximate size of the independent cracks is indicated. Where flex cracks are not shown on road test tires, none were in evidence.

Where data are listed under the heading "Hot Room," it is to be understood that the tires have first been run at room temperature. "Aged" tires have been run at room temperature first. All percentages are calculated from the original 0.25-inch cut and are listed in whole numbers.

No attempt has been made to compare the results obtained with those from various flexing machines available in the laboratory. Furthermore, it is not the interest of the authors to show how to compound to obtain maximum resistance to tread cracking.

Except where definitely indicated as "Road" the data are from tires run on the Bureau of Standards machine.

Conclusions

A practical method of studying tread cracking in the laboratory which gives data comparable with field service results has been presented. The method is not a costly one and permits the investigation of a large number of factors that have a bearing on crack growth and flex cracking.

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Formation of Iodine Pentafluoride. Iodine pentafluoride is formed when iodine is brought into contact with fluorine, but is invariably in admixture with the heptafluoride. According to O. Ruff [*Chem.-Ztg.*, **58**, 449 (1934)] compounds with a lower proportion of fluorine could not be detected. In the presence of oxygen, however, or when the pentafluoride was exposed to moisture, iodine oxyfluoride (IOF_3) could be detected.

Determination of Small Amounts of Glucose, Fructose, and Invert Sugar in Absence and Presence of Sucrose

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The method depends upon the oxidation of potassium ferrocyanide to potassium ferricyanide by ceric sulfate after the ferricyanide has been reduced by the sugars in alkaline solution. The end point of the titration is obtained by using alphazurine G as the indicator. This dye is very sensitive in acid solution to any excess of ceric sulfate, but is not affected as long as any ferrocyanide remains in the solution.

The proposed method was developed and used with pure sugar solutions. In addition, its accuracy was examined when certain buffers and other impurities were present in the reduction mixture. Chlorides and tartrates have practically no effect on the reduction of the ferricyanide by invert sugar, while acetate and citrate buffers slightly affect the reduction. The influence of these buffers may be measured and proper correction made.

In connection with a study of the hydrolysis of very dilute sucrose solutions by invertase, it was necessary to make many determinations of the small amounts of invert sugar (0.5 to 2.0 mg.) which were formed. The methods given in the literature as standard for invert sugar determination were examined and found either inconvenient or inaccurate for making many routine determinations. Colorimetric methods were discarded because of the difficulty in manipulation and in preparing standards of the same composition as the unknown sugar solution. In the case of the copper reduction methods, the minute amounts of cuprous oxide could not be measured easily with sufficient accuracy. The Hagedorn-Jensen (*3*) method, while sufficiently precise, requires very careful manipulation. In that method, alkaline potassium ferricyanide is added to the reducing sugar and the unused ferricyanide is determined by iodine-thiosulfate, the amount of ferricyanide reduced by the sugar being then obtained by difference. Very careful measurements must be made of the volume of ferricyanide added to the reduction mixture, since small errors are apt to double in the final determination of the volume of ferricyanide used; and, in addition, the thiosulfate solution requires frequent standardization.

The present method is comparable to the Hagedorn-Jensen method in accuracy and has the advantage of being a direct method, requiring no great skill in manipulation, and using solutions which are very stable. It determines the reducing sugar by oxidation in alkaline solution with potassium ferricyanide, also employing a modification of the method originally suggested by Gentele (*2*). The ferrocyanide formed in the reaction is titrated, after acidifying with sulfuric acid, with a standard solution of ceric sulfate. Furman and Evans (*1*) have shown that ferrocyanide can be oxidized quantitatively by ceric sulfate. Because of the small quantities of reducing sugars in the reduction mixtures, the amounts of ferrocyanide and ceric sulfate were not sufficient to give sharp color changes at the end point in such titrations. This difficulty is met by the use of an inside indicator, alphazurine G, which is extremely sensitive in acid solution to the least excess of ceric sulfate.

Materials and Solutions

Alphazurine G. This dye was a product of the National Aniline Co. It is listed in the Color Index[1] as No. 712 and is supposed to have the same composition as the following: Neptune Blue, BG, Badische Co.; Brilliant Acid Blue V, Bayer Co.; and Azure Blue V, Kalle Co. Its color change in the presence of ceric sulfate as oxidant is from yellowish green to brown and is very distinct and marked when viewed under a white light, such as is given by a 100-watt stereopticon bulb in an ordinary study lamp. (Alphazurine G is suitable as an indicator for either day or night work, since the color change is accentuated by a white light.) The brown color is not permanent, lasting about 3 minutes when pure potassium ferrocyanide is titrated and from 0.5 to 3 minutes if sugar oxidation products are present in the solution. The color change is so pronounced that it can be detected by any one who has observed it a few times in practice, even with an excess of half a drop (a drop being about 0.015 cc.) of 0.01 *M* ceric sulfate.

Five drops of a 0.4 per cent water solution of the dye as obtained from the National Aniline Co., without further purification, were usually used in each titration. Its stability was tested by titrating definite volumes of potassium ferrocyanide solution with ceric sulfate solution, using solutions of alphazurine G which had been prepared at various times during a period of over 3 years. Practically no difference could be noted.

The oxidation products of the sugars apparently have no effect on the ceric sulfate in this titration. Potassium permanganate may be used to titrate the reduction mixture obtained when reducing sugars are oxidized by alkaline potassium ferricyanide, using alphazurine G as indicator, in the same manner as ceric sulfate. The color change of the indicator is not as good as with ceric sulfate; hence, potassium permanganate was used only with pure glucose in the standardization of the ceric sulfate. The color change of the indicator when potassium ferrocyanide solution is titrated is just as good with permanganate as with ceric sulfate.

Ceric Sulfate. A stock solution of ceric sulfate was prepared from cerous oxalate and standardized against Bureau of Standards sodium oxalate, according to directions given by Willard and Young (*6*). About 6 liters of approximately 0.01 *M* ceric sulfate were prepared by diluting 750 cc. of the stock solution of ceric sulfate (0.08122 *M*) and 300 cc. of concentrate sulfuric acid to 6 liters. This dilute solution was standardized against Bureau of Standards glucose by comparison with results obtained when standard potassium permanganate was used to titrate the ferrocyanide formed in the reduction mixture, and against pure potassium ferrocyanide.

[1] Published by the Society of Dyers and Colourists, 30 Pearl Assurance Buildings, Bradford, Yorkshire, England.

In standardization of ceric sulfate solution against glucose the procedure detailed below was followed. The sugar sample contained 1.5 mg. of glucose in 100 cc. Some reduction mixtures, after acidifying with sulfuric acid, were titrated with ceric sulfate, others with standard potassium permanganate. The concentration of the potassium permanganate as determined by titrating against Bureau of Standards sodium oxalate was 0.00931 *N*.

Table I. Standardization of Ceric Sulfate against Glucose

Date	Ceric Sulfate Solution Required	0.00931 *N* Potassium Permanganate Required
	Cc.	*Cc.*
Nov. 14, 1932	4.09	4.47
Dec. 19, 1932	4.085	....
March 18, 1933	4.08	....

The concentration of the ceric sulfate, calculated by comparison with the permanganate values, using an inverse proportion—X : 0.00931 :: 4.47 : 4.085—was 0.01018 *N*.

In standardization of the ceric sulfate solution against pure potassium ferrocyanide, Baker's c. p. analyzed, the sample of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, was accurately weighed, dissolved in water, and diluted to 250 cc. This solution was then poured into a buret and 15 cc. were withdrawn as used into a 400-cc. beaker, diluted to about 95 cc., and acidified with 5.7 cc. of 4.3 *M* sulfuric acid. It was titrated at once with the ceric sulfate solution, using 5 drops of alphazurine G, 0.4 per cent, as indicator. Some titrations were made with standard potassium permanganate as the oxidant and alphazurine G as the indicator.

Table II. Standardization of Ceric Sulfate against Potassium Ferrocyanide

Date	Potassium Ferrocyanide	Ceric Sulfate Solution		0.00931 *N* $KMnO_4$ Solution	
		Found	Calculated[a]	Found	Calculated[a]
		Cc.	*Cc.*	*Cc.*	*Cc.*
Dec. 20, 1932	0.3622 gram in 250 cc. at room temp.	5.135	5.09	5.56	5.52
Mar. 5, 1933	0.3691 gram in 250 cc. at 20° C.	5.24	5.07	..	..

[a] Calculated for 15 cc. of a constant weight of 0.36 gram of potassium ferrocyanide in 250 cc.

From the above data, the concentration of the ceric sulfate by comparison with the permanganate values—X : 0.00931 :: 5.52 : 5.08—was calculated as 0.01013 *N*. Assuming that the potassium ferrocyanide is pure $K_4Fe(CN)_6.3H_2O$, the concentration of the ceric sulfate was found to be—X : 0.003409 :: 1000 : 338.6 or 0.01006 *N*.

Since the ceric ion undergoes a decrease of 1 in valence when used as an oxidant, normal solutions will be the same as molar and the above concentrations may be expressed as 0.01018 *M*, 0.01013 *M*, and 0.01006 *M*. This 0.01 *M* ceric sulfate solution used in most of the experiments has remained stable for over 4 months. The 0.002 *M* solution of ceric sulfate used in the modified method was prepared by diluting 100 cc. of the 0.01 *M* ceric sulfate to 500 cc. at 25° C.

Buffer Solutions. The pH values of the buffer solutions were determined electrometrically.

Potassium Ferricyanide. Merck's c. p. crystals were used without further purification. Eight grams of the crystals were weighed, dissolved in water, and diluted to 1 liter at 20°. This solution was poured into a Pyrex bottle, the outside of which had received two coats of black paint, and was kept in a dark room. When required, the solution was withdrawn by means of a pipet and transferred to a buret which was also kept in a dark room except when the ferricyanide was being withdrawn. Under these conditions, the potassium ferricyanide solution remained stable for at least 6 weeks.

Fructose. The fructose was prepared from cane sugar by the method of Jackson, Silsbee, and Proffitt (*4*), and recrystallized from alcohol until a 2 per cent solution gave a reading of −4.23° at 25° C. using a 200-mm. tube and mercury light (5461 Å.). According to Vosburgh (*5*), the rotation value of a 2 per cent pure fructose solution under the same conditions is −4.18°.

Glucose. Bureau of Standards, standard sample 41.

Sucrose. Bureau of Standards, standard sample 17.

Description of Method

The following procedure provides for the reduction of alkaline potassium ferricyanide by amounts of glucose, fructose, and invert sugar varying from 0.5 to 2.0 mg. in a total volume of 125 cc. and the titration of the ferrocyanide formed with ceric sulfate, using alphazurine G as the indicator.

Five cubic centimeters of potassium ferricyanide solution (8 grams per liter) were placed in a flat-bottomed 125-cc. Pyrex flask containing 15 cc. of water and 5 cc. of sodium carbonate solution (140 grams of $Na_2CO_3.H_2O$ per liter). The flask and its contents were allowed to stand at 25° for 4.5 minutes. A 100-cc. sample of the sugar solution was added by means of a pipet 1.5 minutes before placing in the bath at 80° C. (Sugar solutions at approximately 25° C. were used to make up the sugar sample to a volume a little greater than 100 cc. so that 100 cc. contained the required amount of sugars.) A small glass stirring rod was inserted in the reduction mixture, which was stirred and then covered with a small glass funnel, the stem of which had been removed. The reduction mixture was placed in a water bath kept at 80° C. and stirred for 1 minute, usually beginning about 10 seconds after placing in bath. After 30 minutes, it was removed to a 25° bath, allowing 30 seconds for making the change, and after about 5 seconds was stirred for 1 minute and left for 4.5 minutes. (The entire procedure required 35 minutes.)

After cooling, the mixture was poured into a 400-cc. beaker. The flask was rinsed three times with 5-cc. portions of distilled water which also were added to the beaker. The contents of the beaker were next acidified with 5.7 cc. of 4.3 *M* sulfuric acid and then titrated with 0.01 *M* ceric sulfate, using a Folin microburet to which a jet tube had been attached which delivered drops of approximately 0.015 cc. The ceric sulfate was added in a rapid succession of drops, with constant shaking, to within about 0.1 cc. of the end point. Five drops of a 0.4 per cent alphazurine G solution were added and the titration was continued by adding the ceric sulfate a drop or fraction of a drop at a time, shaking after each addition, until the color changed from yellowish green to brown.

The titration with ceric sulfate is apparently an extremely rapid reaction and hence permits the ceric sulfate to be added slowly or rapidly without affecting results.

Determination of Glucose, Fructose, and Invert Sugar. Different amounts of sucrose may be used, as the slight effect on the ferricyanide appears in the blank and can be measured. In order to have the proper concentration of sugars, it was found convenient to prepare the solutions as follows:

At 25° C. 40 cc. of the glucose solution contained 1 mg. of glucose.

The fructose solution was prepared in the same way as the glucose solution.

Exactly 0.25 gram of glucose and 0.25 gram of fructose were dissolved in water and diluted so that 20 cc. contained 1 mg. of invert sugar.

The sucrose solution was prepared so that 1 cc. contained 2 mg. of sucrose.

The sugar solutions were often prepared approximately 24 hours before being used.

The volume of 0.01 *M* ceric sulfate in Table III, obtained by subtracting the blank for the reagents from the mean of many determinations, represents definite values for the weights of the sugars as given, under the conditions of the reduction. An accuracy of 0.3 to 0.4 per cent was readily attained with 1 mg. of these reducing sugars. Sucrose does not seem to affect the reduction, since the increase in the amount of ceric sulfate solution required when sucrose is present is fairly constant and is approximately 0.02 cc. for 18 mg. of sucrose. The reduction of the potassium ferricyanide by the invert sugar is practically constant and equivalent under the conditions of the reduction to about 0.545 cc. of the 0.01 *M* ceric sulfate solution per 0.2 mg. of invert sugar.

Table III. Determination of Glucose, Fructose, and Invert Sugar by Proposed Method

Weight of Sugar per 100 cc.		0.01 *M* Ceric Sulfate Required	
Glucose	Sucrose	Volume	Calculated for 0.2 mg. of invert sugar
Mg.	*Mg.*	*Cc.*	*Cc.*
0.5	0	1.365	...
1.0	0	2.735	...
2.0	0	5.44	...
0.5	18	1.385	...
1.0	18	2.75	...
2.0	18	5.47	...
Fructose			
0.5	0	1.37	...
1.0	0	2.75	...
2.0	0	5.48	...
0.5	18	1.395	...
1.0	18	2.78	...
2.0	18	5.50	...
Invert sugar			
0.5	0	1.37	...
1.0	0	2.745	...
1.2	0	3.28	0.535
1.4	0	3.83	0.550
1.6	0	4.37	0.540
1.8	0	4.915	0.545
2.0	0	5.46	0.545
0.5	18	1.395	...
1.0	18	2.765	...
1.2	18	3.305	0.540
1.4	18	3.855	0.550
1.6	18	4.40	0.545
1.8	18	4.94	0.540
2.0	18	5.475	0.535

The sodium carbonate and potassium ferricyanide solutions need not be accurately measured into the reduction flask. The sulfuric acid was added to the reduction mixture from a measuring pipet which was filled to the mark and then allowed to empty. Variation of 1 cc. in the amount of acid gave no noticeable effect.

Practically no effect on the results was noted when the temperature of the bath fluctuated from 80° to 79° C.

The alkali had no effect on the sugars when the order of adding the sugar sample and the potassium ferricyanide was reversed. The sugar solution may be allowed to stand as long as 10 minutes in contact with the alkaline solution before adding the potassium ferricyanide solution and continuing with the reduction.

The volume of the reduction mixture can be varied from 125 to 100 cc. without affecting the results to any extent.

A decrease in the amount of reduction was noted when the reduction mixture was allowed to remain in the cooling bath at 25° C. for 9.5 minutes instead of the usual 4.5 minutes. The alkaline mixture seemed much more susceptible to change than when acidified.

Sugar solutions mixed with sodium carbonate, potassium ferricyanide, and acetate buffer solutions showed practically no change when allowed to stand for 5 minutes, and only a trace of an effect was observed when they stood for 10 minutes. This makes it unnecessary to follow rigidly the direction for adding the sugar sample and the potassium ferricyanide solution to the reduction flask.

Modified Method

When amounts of reducing sugar approximating 0.1 mg. are to be determined, a ceric sulfate solution more dilute than 0.01 *M* should be used in order to obtain comparable accuracy. However, when a very dilute ceric sulfate solution is used, the sharpness of the indicator change is affected because of the large volume (about 150 cc.) of the titration mixture. In order to overcome this difficulty the method was modified by selecting 20 cc. as the volume of the reduction mixture and carrying out the reduction in a special tube. This gives a reduction mixture of less than 40 cc. for titration and 0.002 *M* ceric sulfate solution may be used.

This modified method was applied to the determination of amounts of glucose as small as 0.05 mg. The color change of the alphazurine G is not as permanent as with the 0.01 *M* ceric sulfate, but with care it can be distinguished very sharply with 1 drop of 0.002 *M* ceric sulfate solution. An accuracy of less than 0.8 per cent may be easily attained in the determination of these small amounts of glucose. (For details about this modified method, the reader is referred to the author's thesis.)

Obviously, this modified method may be used with amounts of reducing sugar in the range of the previous method (from 0.5 to 2.0 mg.). However, it is not readily applicable in a series of experiments where the volume of the sugar sample is varied greatly in order to maintain the amount of reducing sugar within fixed limits—determination of invert sugar between 2.5 and 10 per cent of the hydrolysis when sucrose solutions varying from 0.02 to 2.0 per cent in concentration are hydrolyzed with invertase.

Influence of Possible Interfering Substances

Since sugar solutions usually contain buffers or other foreign substances, the accuracy of the determination was examined when certain of these substances were present. By adding such a substance to the reduction flask, carrying out the reduction in the presence of definite weights of sugars, and then subtracting the blank for the reagents including the foreign substance, the total effects of the sugars and foreign substance in terms of cubic centimeters of ceric sulfate are obtained. By comparing these results with the values in Table III for the corresponding weights of the sugars, any influence of the foreign substance is readily apparent.

Impurities apt to be present in sugar solutions which are able to influence the reduction of alkaline ferricyanide (or affect the titration of the ferrocyanide with ceric sulfate and alphazurine G) must either be removed or their effect measured and proper correction made.

Chlorides and Tartrates. These substances were found to be without effect on the reduction of ferricyanide when as much as 10 cc. of 0.1 *M* potassium chloride or sodium tartrate was added to the reduction mixture.

Acetate and Citrate Buffers. Both acetate[2] and citrate buffers with pH values of 3.5 and 4.5 increase the reduction of potassium ferricyanide by invert sugar and this increase is not given by the blank for the reagents (including the buffer). Furthermore, this increase seems to be proportional to the amount of invert sugar present. The citrate buffer at pH 5.75 likewise gives an increase in the reduction, but this increase is practically taken care of by the blank and does not affect the reduction of the ferricyanide by the sugar.

Table IV. Increase in Ceric Sulfate Required in Presence of Buffer Solutions[a]

Weight of Sugar		Excess 0.01 *M* Ceric Sulfate Required				
		Acetate buffers		Citrate buffers		
Invert sugar	Sucrose	pH 4.4	pH 4.59	pH 3.5	pH 4.5	pH 5.75
Mg.	*Mg.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
0.5	18	0.02	0.015	...	...	0.005
1.0	18	0.045	0.045	0.035	0.040	0.005
1.2	18	0.055	0.080	...	...	0.020
1.4	18	0.070	0.090	...	...	0.010
1.6	18	0.080	0.100	...	...	0.015
1.8	18	0.090	0.110	...	...	0.020
2.0	18	0.100	0.135	0.110	0.115	0.025

[a] In each case 10 cc. of buffer were measured into reduction flask and the reduction carried out in the regular way, total volume of reduction mixture being 125 cc.

Probable Applications

The proposed method provides for the determination of small amounts of reducing sugars and because of its simplicity, accuracy, and stability of solutions, may find application in both physiological and general sugar chemistry. By increasing the concentration of the potassium ferricyanide and ceric sulfate solutions, the range of the method as given in Table III may be considerably extended (unpublished data). The period of heating and temperature may be varied to suit specific conditions. Thirty minutes and 80° C.

[2] Two acetate buffer solutions were used: one at pH 4.59 and one at pH 4.4. The one at pH 4.59 was made from sodium acetate and acetic acid and the one at pH 4.4 from sodium hydroxide and acetic acid. The experiments using the buffer at pH 4.4 were run several months after those with the buffer at pH 4.59 and all solutions had been remade except the ceric sulfate. Three citrate buffers with pH values of 3.5, 4.5, and 5.75 were used. These buffers were made from solutions of citric acid, sodium hydroxide, and hydrochloric acid.

were selected because preliminary experiments indicated that the maximum effect of the reducing sugars with little reduction of sucrose was attained under these conditions.

The use of alphazurine G as an indicator for ceric sulfate may find application in the analytical determination of various compounds. Titrations with ceric sulfate and alphazurine G as indicator give constant results with ferrous sulfate, hydroquinone, and potassium ferrocyanide. In the case of potassium ferrocyanide, the results are practically unaffected by phosphoric acid, malic acid, succinic acid, and ethyl alcohol.

Acknowledgment

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The Mackey Oil Tester

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INDUSTRY annually suffers large losses from spontaneous combustion. Despite the seriousness of the hazards encountered in the use of unsaturated oils, satisfactory methods of predetermining the action of such oils have not yet been developed.

Ordinarily, a questionable oil is tested by exposing it to the air on fibers in a heated bath. The temperature rise within a specified time is used as an indication of the degree of hazard of the oil. In the Mackey tester, which is used to the greatest extent, 14 grams of the oil are intimately worked into 7 grams of cotton. This material, with a thermometer in the middle, is then put into a wire gauze and the whole inserted in a combustion chamber, which is merely a water-jacketed container of specified size kept at 100° C. in which arrangement for a continuous current of air is provided by means of tubes inserted in the cover. Any oil which shows a temperature of over 100° C. at the end of 1 hour or over 200° C. at the end of 2 hours is arbitrarily considered as dangerous; results thus obtained seem to agree with practice.

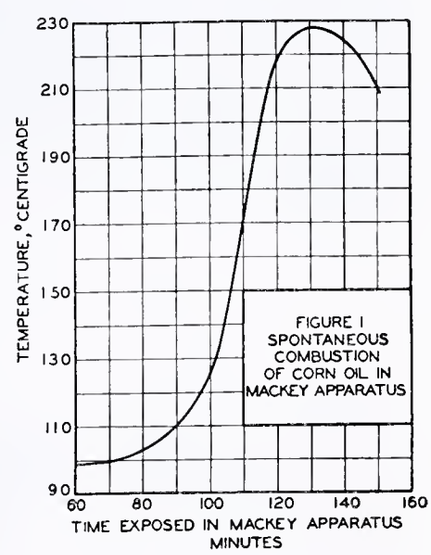
In order to study the action of the tester, samples were carefully prepared in identical manner and subjected to the test. Figure 1 shows a typical curve. Between the times of 95 and 120 minutes there is a temperature rise of 98° or 3.9° C. per minute.

Table I. Tests with Corn Oil

Temperature at End of First hour	Second hour	Maximum Temperature	Time to Reach Maximum
° C.	° C.	° C.	Min.
95	185	205	100
97	180	202	93
100	175	192	100
96	173	178	110
96	170	190	100
96	170	174	110
105	173	190	100
99	140	152	100
95	180	198	100
95	183	198	103
96	171	187	100
95	190	207	110
95	190	206	100
99	165	182	100
104	200	225	100
104	182	203	100

Considerable discrepancies are frequently encountered in the temperature of the samples when duplicates are tested, as is illustrated by the results of the tests on corn oil. No matter how carefully the oil is dispersed through the cotton, there is some difference between the samples. Moreover, factors such as the depth at which the thermometer is inserted, its position in relation to the center of the wire cylinder, the condition of the cylinder itself, whether new or covered with an oily film, and the height of the water bath—all cause variable results, that frequently cause the rise in temperature to vary by as much as 10 minutes. In the case of the oil in Figure 1, this would mean a temperature difference of 39° C. on the steep part of the curve. It may thus happen that a dangerous oil may be considered safe and *vice versa.*

In making these tests, if the oil is not extremely inflammable, a maximum temperature is reached after a quick rise. If the temperatures of the samples are observed only at the suggested times of 1 and 2 hours, it may well happen that the maximum may have been passed and a low temperature would be recorded. A dangerous oil would thus be passed as safe.



In order to make this test more reliable, some standard other than the arbitrary "not over 100° in the first or over 200° C. at the end of the second hour" should be considered. In the many tests conducted, it has been found that the time required to reach a maximum temperature gives better checks and is of much more value in determining the future action of an oil than the usual standard. The actual maximum temperature is of some value in appraising an oil, but considerable discrepancies occur in the numerical values.

It is apparent that the ruling factor to be considered in judging the safety of an oil is the time required to attain the maximum temperature, and not merely the temperature at the expiration of 1 or 2 hours.

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Microanalytical Determination of Carbon and Hydrogen

A Simplified Method

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SINCE the introduction of organic microchemical methods at New York University (*1*) in 1925, the interest in these procedures has widened considerably (*21*, *33*), notably at the University of Pittsburgh, Coal Research Institute, Pittsburgh, Merck's Research Laboratory, Rockefeller Institute, College of Physicians and Surgeons, Columbia University, Loyola College, Baltimore, and elsewhere. A simplified method for the microdetermination of carbon and hydrogen is described below, incorporating numerous improvements.

Apparatus

In the simplified apparatus the use of air has been eliminated from the combustion train and the gasometer is replaced by the use of a reduction valve on the oxygen tank, *a*, and a Pregl precision stopcock (*28*). Traces of organic matter and hydrogen found in many sources of oxygen are eliminated by passing the gas through a preheater, *b*, devised by Böck and Beaucourt (*5*) and modified by Whitman (*36*). It consists of two quartz tubes, one inside the other, the outer one, which is filled with coarse copper oxide or platinum asbestos, being 100 mm. long and 10 mm. in diameter. The inner tube is 3 mm. in diameter, open at the upper end and sealed to the outer tube at the bottom, thence extending 40 mm. downward, a ground-glass joint attaching it to the spiral coil. The preheater is heated by an electric heating cap or by a Bunsen burner, and by cooling the oxygen in the spiral coil possible decomposition of the rubber connections is avoided.

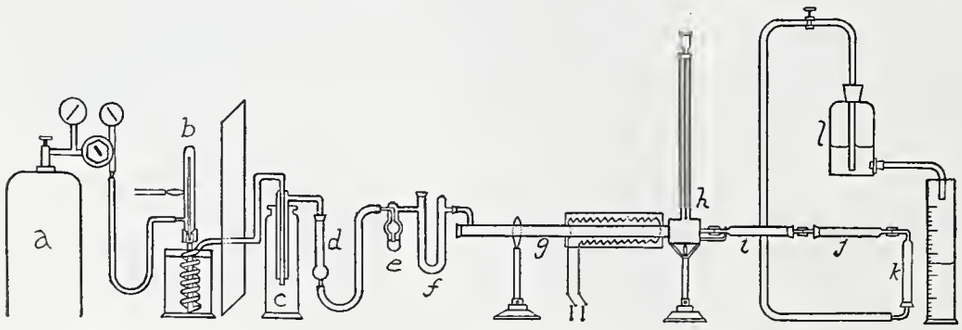

Figure 1. Combustion Train

a. Oxygen tank
b. Preheater
c. Pressure regulator
d. Ascarite tube
e. Bubble counter
f. Drying tube
g. Combustion tube
h. Heating mortar
i. Water-absorption tube
j. Carbon dioxide–absorption tube
k. Drier
l. Mariotte flask

The pressure regulator, *c*, is the usual one described by Pregl (*28*). The side-arm outlet is bent at right angles directly into an ascarite absorption tube, *d*, which also removes moisture, preventing dilution of the alkali in the bubble counter.

The bubble counter, *e*, and drying tube, *d*, are larger than those used by Pregl (*29*). Having a total length of 150 mm. and a diameter of 12 mm., the anhydrone filling needs replacement less often. By connecting the capillary glass arm of the drying tube directly with the side arm of the combustion tube, Pregl's (*29*) capillary tubes and rubber connections are eliminated.

The combustion tube, *g*, is of quartz, 50 cm. long, with a side arm (*24*) of capillary glass of the same dimensions as the arm of the bubble counter. It is filled with the Universal filling devised by Pregl (*30*) and closed by a tight-fitting cork, removable for the introduction of the sample without disconnecting the oxygen stream.

As constant-temperature device, *h*, for the lead superoxide, the improved mortar according to Verdino (*34*) is employed using *p*-cymene as the constant-boiling liquid. A copper rod, protruding from the mortar, heats the capillary constriction on the water absorption tube. The permanent filling is heated by Flaschenträger's (*13*) electric furnace, and a Bunsen burner serves as the movable burner.

Pregl absorption tubes with a hollow ground-glass stopper and well-fitting copper wires suggested by Boetius (*8*) and modified by Whitman (*27*), to reduce the absorption of moisture and carbon dioxide during weighing time, are used. The water absorption tube, *i*, is filled with a coarse and fine layer of anhydrone, previously treated with carbon dioxide, with thick cotton plugs on each side of the layers. The carbon dioxide absorption tube, *j*, contains a 10-mm. layer of anhydrone and is otherwise filled completely with ascarite. They are connected head to head, the water absorption tube next to the combustion tube, with specially impregnated seamless rubber tubing.

The Boyle-Mariotte flask, *l*, is similar to Pregl's (*31*) except for a stopcock on the gas inlet tube, as employed by Lieb. A drier, *k*, filled with anhydrone, attaches it to the absorption tubes.

A similar Mariotte flask is kept in the balance room, serving as an aspirator (*27*) to rinse the oxygen-filled absorption tubes with air while they are cooling to balance room temperature. The air is purified by passing it through a gas wash bottle containing sulfuric acid to remove organic matter, and a purifying tube containing ascarite and anhydrone is connected with the wash bottle. The free end of the water absorption tube is connected with the purifying train and the carbon dioxide absorption tube to the drier of the Mariotte flask, so that the air flows in the same direction as the oxygen during the combustion, bringing the temperature of the absorption tubes quickly down to balance room conditions.

Procedure

1. The capillary ends of the ascarite tube are cleaned with cotton, the copper wires inserted, and the tube is wiped according to Pregl's directions, placed on the rack for 10 minutes, transferred to the balance, and 5 minutes later weighed to 0.01 mg. It is reweighed after 5 minutes. The anhydrone tube is wiped and weighed in the same manner.

2. After removal of the copper wires, the absorption tubes are connected head to head by a rubber tubing 20 mm. long, another 15 mm. long being attached to the anhydrone tube, the rubber tubings having been moistened previously with a trace of glycerol. The absorption tubes are then attached to the combustion train, the anhydrone tube adjoining the latter, and the ascarite tube next to the drier of the Mariotte flask, the side arm of which is always in a horizontal position.

3. The cork stopper of the combustion tube is removed, the substance quickly introduced to within 50 mm. of the oxidation filling, and the tube immediately closed. Then the stopcock to the Mariotte flask is opened.

4. As soon as the gas flow is normal (5 cc. per minute), a small flame is applied 30 mm. from the sample, slowly increased until it envelops the combustion tube, and then gradually moved toward the sample, observing whether the substance sublimes, distills, or decomposes, the distillate or sublimate slowly being driven toward the heated oxidation filling. If it decomposes with charring, it is heated strongly directly under the substance until no black residue remains. The combustion is carried out with 75 cc. of oxygen and should take about 15 minutes, after which it is repeated to burn off all traces of charring, requiring only about 5 minutes.

5. The gaseous products are washed out with 75 cc. of oxygen in 15 minutes, then the stopcock of the Mariotte flask is closed, the absorption tubes are detached and immediately attached to the air filter, and the entire train is connected to the aspirator and washed with 50 cc. of air at the rate of 10 cc. per minute.

By employing two sets of absorption tubes and utilizing the waiting time during the analysis, while washing out the gaseous products, for wiping and weighing the second set, the time for an analysis may be reduced to about 35 minutes.

Discussion

The use of an extra combustion tube for a precombuster, as previously used, incurred the possibility of overheating the rubber connections at the end, but this danger is eliminated by the preheater described above.

Improvements in the Pregl pressure regulator and advice on the treatment of rubber tubing are given by Weygand (*35*). A new pressure meter is also described by Friedrich (*14*). A newer method of treating rubber tubing with strong potassium hydroxide and steaming out has been found effective (*16*).

The original form of the bubble counter was replaced by a few authors with a similarly functioning arrangement. Boetius (*6*) uses a bubble counter having on each side a special removable tube, one filled with ascarite, the other with phosphorus pentoxide–pumice stone mixture.

Pregl's combustion tube has been retained by most authors except Flaschenträger (*12*), whereas Avery, Brackenbury, and Maclay (*2*) suggest the use of copper and silver tubes with water-jacketed ends. Müller and Willenberg (*24*) simplified the handling by devising a side-arm inlet for the combustion tube.

Boetius (*6*), Weygand (*35*), and Lindner (*22*) tested extensively the materials used by Pregl for the filling of the combustion tube. Boetius (*7*) shows in numerous experiments a gradual lessening of the water content of the lead superoxide and Friedrich (*15*) finds that this substance gradually takes up carbon dioxide and gives it off again in the combustion of substances containing nitrogen, halogen, and sulfur. Haas and Rappaport (*17*) suggest cerium dioxide for copper oxide–lead chromate as filling, contending that the tube is better protected. Kirk and McCalla (*20*) use catalytic manganic oxide, and Friedrich (*16*) has devised a catalytic combustion method, permitting the easy removal of the lead superoxide, a platinum foil serving as the catalyst. Niederl (*25*) calls attention to the danger of not having present sufficient oxygen for the complete oxidation, when using this method. In a succeeding article Friedrich (*14*) separates the thermal decomposition of the substance and the oxidation of the decomposition products using the catalyst only for the last, but it seems that combustion would be difficult for substances which char. Attempts have been made to replace the lead superoxide by metallic copper or silver. Lindner suggests air for the actual combustion and nitrogen for the transport gas, but even partial use of air would oxidize the copper and necessitate frequent renewals. Avery, Brackenbury, and Maclay (*2*) use a metal tube allowing the insertion of a copper coil for the combustion of substances containing nitrogen. Niederl and Whitman (*27*) use nitrogen exclusively by mixing the sample with copper oxide and employing a combustion tube filling similar to the micro-Dumas.

Investigations of the weighing errors of absorption tube are summarized by Hernler (*18*) and include the observations of Schoorl (*32*), Friedrich (*15*), Brunner (*10*), and Meixner and Krocker (*23*). Blumer (*4*) and Flaschenträger (*12*) constructed tubes with side-arm exits which could be closed by movable glass stoppers. Mercury for a liquid seal was adopted by Kemmerer and Hallett (*19*) and improved by Cornwall (*11*). Friedrich describes two kinds of mechanically self-sealing tubes (*14*). All these absorption devices have been found of little advantage, as the difficulty of handling (wiping) such tubes increases, while on account of prevented temperature-pressure equalization no greater constancy is observable.

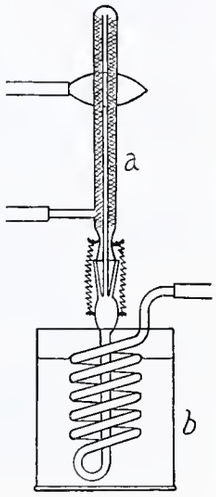

Figure 2. Preheater

a. Preheater tube
b. Condenser

At first moistened soda lime and calcium chloride, as recommended by Pregl (*28*), were used in the absorption tubes which, however, required refilling every six or seven analyses, and ascarite, capable of absorbing up to ten times as much carbon dioxide, was substituted for the soda lime. But when the tube was aspirated, it increased in weight about 0.02 mg. for every 100 cc. of air or oxygen, equivalent to over 0.04 mg. increase for 175 cc. of oxygen and 50 cc. of air used in an analysis and due to the difference in vapor pressure of calcium chloride and ascarite. According to Baxter and Starkweather (*3*) a liter of air passed over calcium chloride and sodium hydroxide contained residual water vapor of 0.36 and 0.16 mg., respectively, indicating that 100 cc. of air dried over fused calcium chloride would give up 0.02 mg. of moisture on passing over ascarite. For this reason anhydrone, a more efficient dehydrating agent, was used.

According to Willard and Smith (*37*), anhydrone is as efficient a drying agent as phosphorus pentoxide. It is neutral, porous, and stable towards heat up to 250° C. Its vapor pressure is 0.000 mm. at 0° C. and it is capable of absorbing water up to 30 per cent of its weight. Kirk and McCalla (*20*) reported using ascarite and anhydrone and Boetius (*9*) ascarite and phosphorus pentoxide. A change in the absorption of the combustion products is described by Niederl and Meadow (*26*). The absorption of carbon dioxide takes place in a filter tube and is gravimetrically determined as barium carbonate.

In previous attempts to eliminate the use of air in the combustion, Müller and Willenberg (*24*) and later Kirk and McCalla (*20*) weigh the absorption tubes filled with oxygen instead of air. Later experiments on absorption tubes which are not self-sealing show that they cannot be brought to constant weight when filled with oxygen, and self-sealing tubes, as mentioned before, do not allow for the equalization of pressure and temperature of the contained oxygen or air to balance room conditions. Table I shows the decrease in weight of the absorption tubes on standing, due to the replacement of oxygen by air, comparing also the increase in

weight when filled with air due to the absorption of moisture and carbon dioxide, with and without wires in the capillaries.

TABLE I. CHANGE IN WEIGHT OF ABSORPTION TUBES

(Measured in 0.001 mg.)

	Anhydrone Minutes			Ascarite Minutes		
	15	45	90	15	45	90
Filled with oxygen						
Without wires	−47	−104	−168	−23	−76	−125
With wires	− 9	− 41	− 88	−13	−37	− 82
Filled with air						
Without wires	+ 3	+ 11	+ 19	+ 3	+ 6	+ 13
With wires	+ 2	+ 4	+ 9	+ 1	+ 4	+ 8

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Determination of Selenium and Arsenic by Distillation

In Pyrites, Shales, Soils, and Agricultural Products

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INVESTIGATION of an animal disturbance (known locally as alkali disease), which was traced to vegetation grown in certain soil areas, rendered urgent the development of a rapid and accurate method for the detection and estimation of selenium in both organic and inorganic materials. The methods outlined below are an extension and improvement of a distillation method described by Robinson (*7*) during the progress of the work.

The principles of the distillation method are outlined by Noyes and Bray (*6*). Selenium can be separated from all the other elements except arsenic and germanium by distillation with concentrated hydrobromic acid. The selenium must be in, or be converted into, the hexavalent condition before distillation in order to insure its distillation with the acid. In most cases this conversion may be accomplished by the use of bromine. The excess of bromine distills at a low temperature and the hydrobromic acid then reduces the selenium to the quadrivalent condition. In this form it readily distills along with hydrobromic acid.

When a distillation method is applied to soils and other insoluble materials difficulties due to bumping and frothing may be encountered. Bumping may be greatly minimized by the introduction of short pieces of capillary tubing, sealed at one end. In the case of soils, at least, frothing is diminished or wholly prevented by the use of a sufficient excess of bromine.

In the distillate, selenium may be precipitated quantitatively by reduction by sulfur dioxide and hydroxylamine hydrochloride. The selenium may be estimated either gravimetrically or by the colorimetric procedure of Cousen (*2*). In either case reprecipitation is essential to free the precipitate from sensible quantities of impurities.

Arsenic is quantitatively distilled along with the selenium and may be determined in the filtrate from the first selenium precipitation. If present in but small quantities it is best determined by one of the modifications (*3*, *9*) of the cerulean blue molybdate method of Denigés (*4*).

In general, the procedures described below are very sensitive and may be used for any material with such modifications as may be necessary. The method as developed for soils is perhaps the most sensitive used in soil analysis. One part of selenium in ten million parts of soil may be easily detected and by use of the integration procedure described below, quantities as small as one part in a billion may be isolated.

APPARATUS

A distilling apparatus is graphically described in Figure 1. The still is conveniently made of Pyrex glass and rubber connections must be avoided. Measuring flasks and Nessler jars of 25 cc. capacity are also required.

REAGENTS

All reagents should be free from selenium. Blank determinations should be made on all reagents.

1. Hydrobromic acid, 40 to 48 per cent, capable of being completely decolorized with sulfur dioxide.
2. Bromine.
3. Solution of 1 cc. of bromine in 10 cc. of hydrobromic acid.
4. Hydroxylamine hydrochloride.
5. Sulfur dioxide as compressed gas in cylinders.
6. Five per cent solution of gum arabic in water.
7. A suspension of asbestos which will not lose weight when washed with strong hydrobromic acid.

Procedure for Soils

The air-dried sample should be well mixed and passed through a 2-mm. sieve.

Weigh out 50 grams of the air-dried soil and transfer to the distilling flask. Add 10 cc. of solution 3, a few cubic centimeters at a time, with shaking. If carbonates are present, add the mixture to the contents of the flask slowly and with constant shaking to avoid loss by frothing. Add, in all, 10 to 50 cc. of solution 3, the quantity depending on the quantity of organic matter present. There must be an excess of bromine over that required to saturate the organic matter in the soil. After sufficient bromine in solution 3 has been added, add enough hydrobromic acid to bring the total quantity of this reagent up to 75 to 100 cc. The larger quantity is used on soils containing much calcium carbonate or on very basic soils. Connect the still with the adapter just below the surface of 2 to 3 cc. of bromine water in the receiver flask and apply heat gradually. One or two grams of bromine should distill over in the first few cubic centimeters of distillate. If insufficient bromine has been added to produce this quantity of bromine, more must be added. A somewhat greater excess of bromine does no harm, but too great an excess is to be avoided because of the formation of too much sulfuric acid later. When danger of frothing is passed, apply increased heat and collect from 30 to 50 cc. of distillate. Make a second, or even third, distillation with intervening additions of hydrobromic acid and bromine, unless it is certain from experience that all the selenium is in the first distillate. Remove the distillate and pass in sulfur dioxide until the yellow color due to bromine is discharged. Add 0.25 to 0.5 gram of hydroxylamine hydrochloride, stopper the flask loosely, put on the steam bath for an hour, and allow to stand overnight at room temperature. If selenium is present it will appear as a characteristic pink or red precipitate. If much selenium is present it will shortly turn black.

Collect the precipitated selenium on an asbestos pad in a porcelain crucible, and wash slightly with hydrobromic acid containing a little hydroxylamine hydrochloride. Dissolve the selenium on the pad by passing through 10 to 15 cc. of solution 3 in small quantities and wash into a 25-cc. measuring flask if the quantity is small and is to be estimated colorimetrically. If over 0.5 mg., filter into a small beaker, precipitate as before, gather on an asbestos pad as before, and wash with hydrobromic acid containing a little hydroxylamine hydrochloride and then with water. Prepare a tare in a similar manner. Dry at 90° C. for 1 hour, place in a vacuum desiccator, and exhaust the air while the crucibles are still hot. Cool 0.5 hour. Allow the air to enter the desiccator, cool an additional half-hour, and weigh against a tare. Check the weight by drying again. If the quantity is small and is to be estimated colorimetrically, add 1 cc. of a solution containing 5 per cent gum arabic and precipitate the selenium by sulfur dioxide and hydroxylamine hydrochloride. Prepare comparison solutions containing known quantities of selenium in exactly the same manner and allow them to stand overnight. Shake the standard and test solutions and compare the depth of color in Nessler jars. This comparison is best carried out in sunlight. It is difficult to match solutions containing more than 0.5 mg. of selenium in 25 cc. and the color comparison is most satisfactory when 0.01 to 0.1 mg. is present.

Procedure for Pyrites and Other Sulfides

Grind the sample to pass a 100-mesh sieve. Weigh out 10 grams of the sample. Pour 100 cc. of concentrated nitric acid into a 300-cc. quartz or porcelain dish and place the dish on the steam bath. Add small portions of the pyrites into the dish by tapping from a spatula, stir thoroughly between portions, and add more when brown fumes cease to come off. Add 25 to 50 cc. more nitric acid when half the material has been added. When the reaction appears to be complete, add 15 cc. of concentrated sulfuric acid and evaporate until all nitric acid is expelled. Add a few drops of 30 per cent hydrogen peroxide and stir vigorously. When the peroxide is decomposed add 75 cc. of concentrated hydrobromic acid and bromine and distill as under directions for soils. The mixture bumps badly.

Procedure for Water

Measure from 1 to 10 liters of water, and add sufficient sodium peroxide to make the liquid definitely alkaline. Evaporate to dryness. Take up with 100 cc. of concentrated hydrobromic acid and 1 to 5 cc. of bromine, depending upon the quantity of organic matter present, and proceed as under directions for soils.

Procedure for Vegetable Matter

With vegetation the procedure must be modified according to the quantity of selenium present. The most satisfactory procedure for material of unknown character is as follows:

Stir 100 grams of well ground and mixed vegetation into a concentrated solution of 25 grams of magnesium nitrate, and add 5 grams of magnesium oxide. Dry the mass over a water bath and finally in an oven at 105° C. Ignite the dried material slowly in a muffle until the ash is a uniform gray color.[1] After ignition, triturate the ash with 100 cc. of concentrated hydrobromic acid and 2 cc. of bromine, transfer it to a distilling flask, distill as suggested for soils, and estimate the selenium in the distillate.

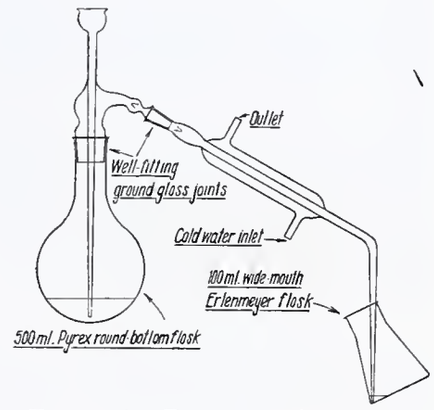

Figure 1. Distilling Apparatus

In case the quantity of selenium exceeds 2 parts per million it is preferable to use a procedure devised by A. Van Kleeck in this laboratory. The procedure is as follows:

Digest 1 to 5 grams of the material with sulfuric acid as in the Kjeldahl process, using a suitable catalyst. Instead of digesting in a Kjeldahl flask, carry out the process in the distillation apparatus previously described (Figure 1). Conduct the issuing gases through bromine water which is kept continuously supplied with an excess of bromine. When the digestion is complete, cool the flask and cautiously add an equal volume of water and then the distillate, together with 100 cc. of concentrated hydrobromic acid, through the funnel of the distilling apparatus. Distill the mixture, as in the case of soils, and estimate the selenium. If more than 5 grams of vegetation must be digested in order to secure a measurable quantity of selenium, this procedure becomes very tedious, but it nevertheless seems to be the most accurate yet devised. The oxidation of vegetation, preliminary to distillation, may also be effected by digestion with 30 per cent hydrogen peroxide to which has been added 0.5 gram of soil and a few drops of nitric acid.

Procedure for Animal Tissue

Cut flesh, skin, etc., into small pieces and drop into cold 30 per cent hydrogen peroxide. When danger of frothing has ceased, warm on the steam bath, add a little nitric acid, and when decomposition is nearly complete, add about 5 per cent of the weight of the sample of magnesium nitrate. Evaporate to dryness and char at a low temperature. The animal tissues may also be digested by the Kjeldahl process as a preparation for distillation if the selenium content is sufficiently large. Distill and proceed as under "Soils."

Sensitiveness of Method

By the use of what may be termed an integration distillation process (the cohobation of the alchemist) the selenium from a large quantity of soil may be concentrated into a very small volume of distillate. A charge of 50 to 100 grams of soil or plant ash is distilled and the distillate is poured back

[1] Beath (*1*) and his associates at the University of Wyoming use a procedure which they ascribe to Taboury (*8*) but with a very important modification. The material is digested with a solution of sodium hydroxide, dried, and ignited to a gray ash. During this ignition a very voluminous swelling occurs, accompanied by crust formation which makes the procedure difficult. Ignition without the addition of a fixative is accompanied by large losses of selenium. Even with this addition the loss of some selenium remains possible.

into the still with a fresh sample of soil with additional hydrobromic acid and bromine, and the process repeated.

Fifty grams of Cecil sandy loam from Statesville, N. C., were treated with 75 cc. of 42 per cent hydrobromic acid and 2 cc. of bromine, and distilled until the volume of the distillate measured was about 50 cc. One hundred grams of a fresh sample of the soil were introduced into the flask, the distillate from the first lot was poured into the distilling flask, 75 cc. of hydrobromic acid and 2 cc. of bromine were added to the mixture in the flask, and the contents distilled until the volume of the distillate was again about 50 cc. One hundred grams more of the soil were put in the distilling flask and the operation repeated as above. The residual soil from each distillation was, of course, thrown away. In this manner the selenium in 250 grams of soil was concentrated into a distillate of about 50 cc. This was further concentrated in a small still to about 10 cc. This distillate, when treated to precipitate the selenium, showed the presence of about 0.02 mg. of selenium as estimated colorimetrically, or 0.08 part per million, on the soil basis. The reagents yielded no blank test. Carrington loam from Winthrop, Iowa, and Colby silt loam from Hays, Kans., showed the presence of about the same quantity of selenium.

Five hundred grams of Norfolk fine sandy loam treated in five 100-gram lots, as outlined above, gave no test for selenium. To 1000 grams of this soil 0.002 mg. of selenium in the form of a solution of sodium selenate was added. After drying, it was treated with hydrobromic acid and bromine in 10 lots of 100 grams each by the integration distillation process and a distinct red precipitate on the bottom of the small glass tube resulted, corresponding to 2 parts per billion.

The recovery of the selenium from the soil appears complete. One-half the quantity of selenium used will give a distinct precipitate under the proper conditions and less than one-tenth as much will give a distinct yellow color when treated, in volumes of 5 cc. or less, by Cousen's (*2*) method, as used in the determination of selenium in glass. The method appears capable of detecting one part of selenium in a billion of soil, and probably with care and patience one part in ten billion can be detected. The limits of detection would be the patience of the analyst in making the number of distillations necessary. Large quantities of the reagents can be prepared free from selenium by redistillation, so there should be no danger of contamination from this source. In carrying out the successive distillations air-dry soils should be employed and no water added to the receiving flasks. This precaution is essential in order to avoid dilution of the successive distillates.

Accuracy of Method

It appears that selenium is quantitatively recovered, by the distillation process, from material properly prepared for distillation. Quantities of selenium as small as 0.01 mg. may be satisfactorily determined colorimetrically. For quantities greater than 0.5 mg. the degree of accuracy with which the precipitated material can be determined depends primarily on the accuracy of the balance employed. When ignition methods are employed there is, of course, a possibility of loss of selenium, despite the fact that added sodium selenate may be quantitatively recovered from wheat and similar materials. Complete combustion of wheat, without the addition of any fixative, reduces the quantity of selenium recovered. In an earlier publication (*7*), it was stated that, in the absence of tellurium, the distillation procedure could be eliminated, and determination made directly upon the leachate from the ash. Unless a second precipitation is made the results so obtained are too high, owing to contamination with silica and possibly other materials.

In the treatment of soils and shales and ignited organic matter some difficulty has been caused by failure to add sufficient bromine to insure an excess.

The agreement of duplicates and of different analysts on the same sample is shown in Table I for two materials, selected because representative of a long series of shales, soils, and grains.

Table I. Agreement of Duplicates and of Different Analysts by Distillation Method

Analyst	Shale, B-2885	Pierre Clay Loam, B-391	Wheat
	P. p. m.	*P. p. m.*	*P. p. m.*
H. C. Dudley	32–35	10–12	15–15[a]
W. O. Robinson	38–40	11–14	14[b]–17[c]
K. T. Williams	38–40	10–11	14[a]–16[1a]

[a] Oxidation by Kjeldahl process.
[b] Ignition with magnesium nitrate.
[c] Oxidation with hydrogen peroxide.

Determination of Arsenic

In the process of isolation of selenium any arsenic present in the sample distills over with the hydrobromic acid and is converted into arsenic acid by the bromine present in the receiver. Reduction by sulfur dioxide and hydroxylamine does not precipitate the arsenic, which is present quantitatively in the first filtrate from the selenium precipitate. It is thus separated from all other elements save germanium. A quantitative separation of all the arsenic from mispickel was effected by one distillation when the mispickel was treated as recommended for pyrites. Arsenic may be determined in the filtrate from the selenium determination after evaporation with concentrated nitric acid, essentially as recommended by Deemer and Schricker (*3*) for the determination of arsenic in plant ash. By the use of the integrated distillation procedure the detection and estimation of arsenic may be made as sensitive as is the case with selenium.

The same procedure may be followed for concentration of germanium into the distillate where it appears in the filtrate after removal of selenium. In the solution it may be determined by the methods suggested by Noyes and Bray (*6*) or Hillebrand and Lundell (*5*). In the present investigation, no attempt has as yet been made to apply the procedures suggested to the determination of germanium. The procedure suggested for arsenic was followed in the case of a sample of Cecil clay loam from North Carolina, and 21 parts per million found.

The method described, with appropriate modifications, has been applied to the determination of selenium in several thousand analyses in this laboratory and has been found eminently satisfactory. These analyses include the estimation of selenium in sulfide ores, shales, soils, water, a wide range of vegetation and grains, blood, hoofs, bones, and a wide variety of animal tissues. The quantities found have ranged from minute fractions of a part per million to as high as 0.38 per cent.

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AB CO

Determination of Total Carbon in Soils by the Wet Oxidation Method

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The apparatus presented obviates the necessity for glass seals to prevent contamination of the sample by the disintegration of rubber connections. A novel but efficient interception of the fumes from the oxidizing solution allows complete absorption of the carbon dioxide. The use of a measured quantity of absorbing solution permits a single titration with phenolphthalein as the indicator with the elimination of the methyl orange titration except when desired as a check. Twelve units occupy but 6.5 feet of desk space.

The need of a rapid method for the determination of carbon is apparent when a large number of samples are to be analyzed. In the investigations under way at this station experimental plots are sampled periodically and are analyzed for carbon to obtain an index of the changes in the organic matter content of the soils as influenced by the crop management.

The methods for the determination of carbon in soils are well known. The carbon, regardless of form or source, is converted into carbon dioxide which in turn is determined by gravimetric, titrimetric, or gasometric methods. The furnace or dry combustion method is ordinarily employed and consists of the oxidation of the carbon by oxygen at a high temperature. A mixture of sulfuric and chromic acids has been used extensively for this purpose in the so-called wet combustion method. The fact that the two methods give comparable results has been established by Ames and Gaither (*1*) and White and Holben (*11*); the former found it necessary to boil the solution in order to obtain complete oxidation of the carbon, while the latter introduced the use of an absorption tube containing constant-boiling sulfuric acid to intercept the fumes from the boiling solution, thus insuring complete absorption of the carbon dioxide. Other workers, Cameron and Breazeale (*3*), Brown (*2*), Hardy (*4*), Heck (*5*), and Schollenberger (*8*), have studied the wet oxidation method as applied to soils. A variation of the method is that of Robinson (*7*) in which the sulfur dioxide evolved in the Kjeldahl digestion of soil was used as a measure of the carbon content. The results were low as compared with those obtained by the furnace method; therefore a factor was used to correct for the deficiency. Some modification is necessary when the method is applied to materials containing chlorides. Normal soils do not contain these in appreciable quantities; consequently the apparatus as presented does not take these into account.

Brown used the soil residues following the determination of carbon by the wet oxidation method for the determination of nitrogen. The results were in fair agreement as compared with those obtained by the Gunning method. The apparatus presented was developed with the idea of saving time and materials. However, the speed with which the carbon determination can be made, coupled with the difficulties involved in the removal of the excess sulfuric acid before making the Kjeldahl distillation, made this procedure unnecessary and undesirable.

White and Holben point out the danger of contamination of the sample by the charring and disintegration of rubber stoppers through contact with the fumes from the oxidizing solution. They used the Knorr apparatus in which glass seals instead of rubber stoppers are employed. It has been found in this laboratory that contamination from the source mentioned is very appreciable after a few determinations are made. This objection, coupled with the cost of equipment using glass seals, led to the abandonment of the type of apparatus ordinarily used and the development of a unit that can be prepared at a low cost. It is very compact, easy to operate, and in addition retains the features necessary for accuracy. Rubber stoppers can be used safely. The incoming oxygen prevents the fumes from reaching the stopper of the Kjeldahl flask, while the interception of the fumes by the glass wool protects the smaller stopper. The necessity of using a condenser to return the acid and water to the oxidizing solution is eliminated. The fumes are intercepted in a novel but efficient way which allows the complete absorption of the liberated carbon dioxide.

Construction of Apparatus

Oxygen Line. This consists of 0.375-inch (0.94-cm.) copper tubing into which the individual 0.125-inch (0.3-cm.) copper outlets are soldered at intervals of 6.25 inches (15.6 cm.). Glass tees and rubber tubing have been used but are more difficult to support.

Modified Bunsen Valve (Figure 2). A 3-inch (7.5-cm.) piece of glass tubing is fitted at each end with a rubber stopper carrying a short piece of glass tubing. The valve consists of a 1-inch (2.5-cm.) piece of thin-walled, red rubber tubing in which a smoothly cut slit, 0.125 to 0.188 inch (0.31 to 0.47 cm.) long, is made. The valve is attached to the glass tubing of one of the stoppers and the free end plugged with a short piece of glass rod, the mounted valve being enclosed in the 3-inch (7.5-cm.) glass tube.

Absorption Tube. Pyrex, heavy-walled tubing of an outside diameter equal to the average inside diameter of 800-cc. Kjeldahl flasks is used. A length equal to that of the neck of the flask is constricted to approximately 1 cm. at one end. This is packed with glass wool to within 1 inch (2.5 cm.) of the open end, care being taken to leave no channels. If packed too firmly the gases from the oxidation flask will be forced back into the main line in spite of the Bunsen valve and will be distributed among the units of lower resistance. The wool has to be changed after approximately one hundred determinations, as it disintegrates under prolonged acid digestion.

Delivery Tube. This is made from 10-mm. Pyrex combustion tubing. The added strength of the heavy wall is necessary to prevent excessive breakage.

Carbon Dioxide Absorption Tower. This is a modified Truog (*10*) tower. The lower end is constricted to insure the formation of a stream of small bubbles and to retain the short pieces of glass tubing which are not removed during the washing process.

Operation of Apparatus

Sulfuric acid is boiled in each unit for 10 to 15 minutes to saturate the glass wool preparatory to operation. This suffices for the life of the wool. An amount of sample sufficient to produce 0.1 to 0.3 gram of carbon dioxide is added to *G*, care being taken to prevent any of the sample from adhering to the neck of the flask. Three to five grams of potassium dichromate are added to the dry sample and *G* is clamped loosely in position. Approximately 60 cc. of concentrated sulfuric acid are now added from a flask with wash-bottle fittings, using compressed air or oxygen. The entire assembly, including the measured quantity (100 cc.) of sodium hydroxide in flask *K* which has previously been attached to stopper *J*, is connected to flask *G* at *E*. The oxygen inlet tube *A* which is attached to the main line (not shown) is of

sufficient length to allow the assembly to hang on a universal clamp attached to the upper part of the rod before making the connection and while the apparatus is not in use.

It is best to regulate the flow of oxygen, or air, for each unit before heating is commenced. This is done by means of the screw-clamp on *A*. The upward or downward adjustment of the absorption tower is made at this time; this is made easier by lubricating the openings in stopper *J* with glycerol, as recommended by Heck. The flow of oxygen is now shut off at the tank, spring clamp *C* is placed on the rubber tube between the valve and glass inlet tube *D*, and slow heating is begun. Slow boiling is continued for 15 minutes and then *C* is clamped on *D* and oxygen is forced through all the units simultaneously with sufficient force to maintain a rapid flow of bubbles in the absorption towers.

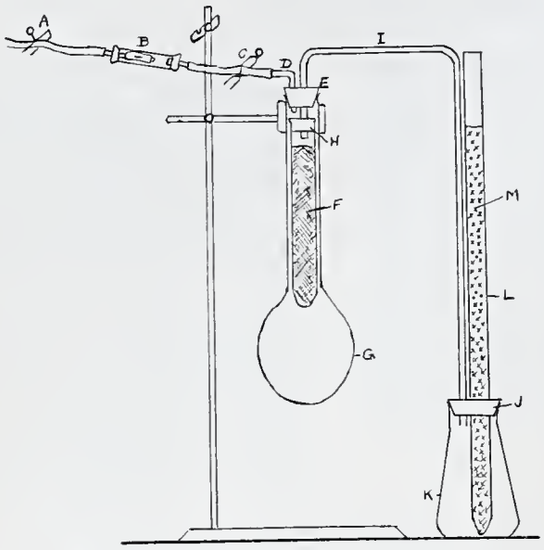

FIGURE 1. DIAGRAM OF APPARATUS

A. Rubber tube leading to main oxygen line with screw pinch clamp
B. Modified Bunsen valve
C. Spring pinch clamp
D. Inlet tube for oxygen
E. No. 7 rubber stopper
F. Tube with glass wool
G. Kjeldahl digestion flask, 800 cc.
H. Rubber stopper for *F* attached to *I*
I. Delivery tube
J. No. 10 rubber stopper
K. Erlenmeyer flask, 500 cc.
L. Absorption tower
M. Glass tubing as beads

When the oxidation is complete (30 to 45 minutes) the oxygen is shut off, *C* is clamped on the rubber inlet tube, the absorption flasks are loosened, and heating is discontinued. The apparatus is elevated with one hand and the tower flushed with approximately 150 cc. of water, the last 20 cc. being used to wash the outside of the tip of the tower. The entire apparatus is now clamped in an elevated position and left until cool.

Twelve units can be operated satisfactorily from one tank of oxygen, using a pressure regulator. Air under constant pressure and free from carbon dioxide can be used. Drawing air through the apparatus is not recommended, as the vacuum produced decreases the absorptive capacity of the glass wool.

DETERMINATION OF CARBON DIOXIDE

A comprehensive survey of the literature on the determination of carbon dioxide is given by Partridge and Schroeder (*6*).

There are two titrimetric procedures ordinarily used when the carbon dioxide is dissolved in a solution of either sodium or potassium hydroxide. One is to titrate with a standard acid using phenolphthalein and methyl orange as the indicators, the former indicating the complete neutralization of the base and the conversion of the carbonate to bicarbonate; the latter indicating the conversion of the bicarbonate to a salt, carbon dioxide, and water. In the other procedure a measured quantity of base is used to absorb the carbon dioxide, the carbonate is precipitated as barium carbonate, and the solution titrated to the phenolphthalein end point. A like quantity of base is titrated to the same end point and is termed the blank. The difference between the titrimetric value of the blank and sample solution is proportional to the amount of carbon dioxide absorbed from the sample. Heck terms this a "single" titration, while Schroeder calls it the Winkler titration. This use of a measured quantity of base to absorb the carbon dioxide from a sample, with a like quantity as a blank, makes unnecessary the titration of the solutions beyond the phenolphthalein end point, even though the carbonate is not precipitated as barium carbonate. The titrimetric value of the blank minus that of the sample solution gives a difference that is proportional to the amount of the carbon dioxide absorbed, as is the case in the Winkler titration. This difference, numerically, is twice that for the Winkler titration if the same strength acid is used in both cases; it follows that the carbon equivalent of the acid in the first case is one-half that used in the Winkler method. This difference is also equal, numerically, to the amount of acid required to titrate the sample solution from the phenolphthalein end point to the methyl orange end point, providing the blank has also been titrated to the same end point to determine the amount of carbonate it contains. In this procedure one titration serves as a check on the other. This technic has been used for several years in this laboratory and has been found reliable.

Truog has given a discussion of the difficulties involved in the so-called double titration. Schroeder (*9*) gives a critical discussion of the conditions pertaining to an accurate analysis of a mixture of base and carbonate. The phenolphthalein end point is quite definite, however, if the solution is agitated by a mechanical stirrer so that the operator's attention can be centered on the color change. Mechanical stirring is also an aid should the methyl orange titration be made.

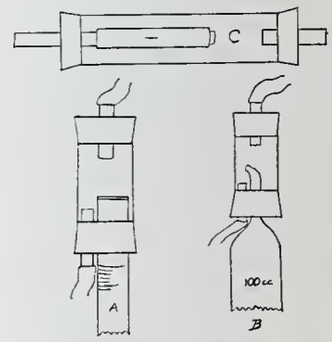

FIGURE 2. DETAILS OF APPARATUS

A. Top section of buret (three-way stopcock)
B. Top section of automatic pipet modified to deliver solution under pressure
C. Modified Bunsen valve

The complete absorption of carbon dioxide from a rapidly flowing stream of oxygen and this gas requires a fairly strong solution of sodium hydroxide. Ames and Gaither, and Brown used a 4 per cent solution for this purpose. This method employs 100 cc. of an approximately 0.5 *N* solution. The titration of a large excess of unused base is exceedingly laborious if an acid sufficiently dilute to insure an accurate end point is used alone. To obviate this difficulty it is necessary to know the approximate carbon content of the sample.

A measured quantity of approximately 2.5 *N* acid, sufficient to neutralize most of the base unused by the carbon dioxide, is added from a buret to the sample solution accompanied by stirring or vigorous rotation of the flask. The solution is then titrated to the phenolphthalein end point with the weaker acid. To another 100-cc. portion of the base a like amount of strong acid is added and titrated in the same way; this is termed the blank. The difference obtained by subtracting the titrimetric value of the sample solution from the blank is then multiplied by the carbon equivalent of the titrating acid. The accuracy of this procedure is determined by that with which the solutions are measured. The chance for error is enhanced by the considerable variation in the strengths of the solutions used. A satisfactory and rapid procedure is to use an automatic pipet to dispense the sodium hydroxide and a buret with a three-way stopcock for the strong acid. Each is so equipped (Figure 2) that the entire contents can be forced out with carbon dioxide–free air under pressure; the air being allowed to flow through each for an instant to sweep the tips free of solution. The titrations of dupli-

cate blanks with a 0.166 N acid show that a combination of the factors involved results in an average error of 0.3 mg. of carbon.

It is not necessary to have the approximately 0.5 N sodium hydroxide free from carbonate. Neither it nor the strong acid needs to be standardized. The saving in time is considerable and is enhanced if large quantities are prepared at one time, as is desirable for routine work. A considerable saving of the standard acid is accomplished in the use of the single titration if the proper amount of strong acid is used for establishment of the blank.

Table I. Comparison of Dry Combustion and Wet Oxidation Methods

Substance Analyzed	Total Carbon Wet oxidation	Total Carbon Dry combustion
	%	%
Soluble starch	36.86	36.89
Potassium acid phthalate	44.64	44.45
Soil 188[a]	2.01	1.98
Soil 199[a]	2.04	2.05
Soil 4	1.00	0.99
Soil 7B	0.39	0.40
Soil 4C	0.58	0.58

[a] Samples furnished by E. C. Shorey, Bureau of Chemistry and Soils, Washington.

Analytical Data

Although the apparatus was developed for the determination of carbon in soils, it has been used to determine its adaptability to a limited number of other materials. The apparatus needs modification for use with some organic materials, as the reaction with the oxidizing solution is very vigorous. As presented it is best adapted to materials of medium to low carbon content. A comparison of results obtained by the dry combustion and wet oxidation methods is made in Table I.

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Constant-Head Gas Scrubber for Small Pressure Drops

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In the analysis of combustible gases by thermal conductivity, it is often necessary to eliminate one or more constituents by combustion and subsequent removal of the combustion products. In such a process, particularly if oxygen or air is added for combustion, constant gas flows are essential. To obtain constant rates of flow, the pressure drop through the apparatus must remain unchanged. It is, furthermore, desirable to have as small a gas volume and pressure drop throughout the apparatus as is consistent with satisfactory operation.

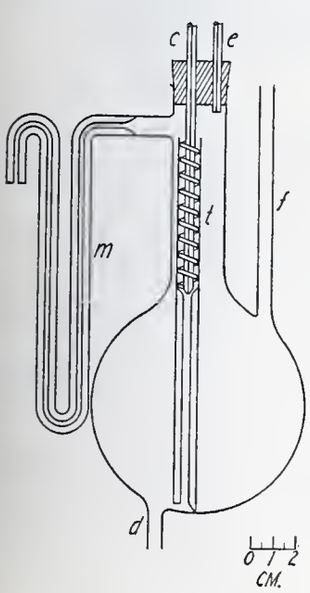

Figure 1

Of the combustion products, water offers no difficulties in removal. Furnas (*1*) has described a gas bubbler which is suitable for carbon dioxide removal by caustic solutions but which has the disadvantage of the possibility of a change in liquid head due to dilution from absorption of moisture and from the carbon dioxide reaction. During the construction of an apparatus for continuous analysis of helium (*3*), now in use in the Amarillo Helium Plant of the U. S. Bureau of Mines, the need arose for a carbon dioxide scrubber to fulfill the requirements outlined above. Such a scrubber has been designed which gives entire satisfaction, and which may find application in similar work.

The gas scrubber, constructed on the principle of the Milligan (*2*) absorber, is shown in Figure 1. It is made from a 500-cc. round-bottomed flask by sealing a manometer tube m to the neck of the flask about 1 cm. below the stopper bottom. The absorbing solution is filled and drained conveniently through tubes f and d, sealed to the side and bottom of the flask. The gas enters through capillary tube c and is scrubbed free from carbon dioxide as it passes upward through the liquid around the spiral which fits snugly in tube t. The spiral is formed from a 2-mm. glass rod wound around the gas inlet tube and fused to it, at each end and in the middle, to secure the rod in place. The gas, as it breaks into bubbles at the entrance to the spiral, creates a lifting effect which causes fresh solution from the bottom of the flask to rise in tube t and pass around the spiral so that a fresh absorption surface is continually presented to the gas. Increase in pressure head, due to dilution, is eliminated by overflow from manometer tube m, by which a constant level is maintained in the flask. The residual gas leaves the flask through capillary tube e.

The scrubbing surface of the spiral is equivalent to a column of solution approximately 20 cm. long. Complete removal of carbon dioxide has been accomplished, using 20 per cent sodium hydroxide solution, from 1.5 liters per hour of gas containing 70 per cent carbon dioxide, for 24- to 30-hour periods. The rate of gas flow is limited by the size of the spiral. The dimensions, as given, provide for a maximum flow of about 3 liters per hour.

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Application of Enclosed Torch to Estimation of Arsenic in Foods

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THE method of the Association of Official Agricultural Chemists (*1*) for the determination of traces of arsenic in foods provides for the destruction of organic matter by wet combustion with nitric and sulfuric acids. Wet ashing, properly conducted, gives concordant results and good recoveries on most food products. In applying it to dried shrimp and cod liver oil, however, the authors experienced certain difficulties, which, together with the long time required for the digestion, led them to try combustion in the enclosed torch devised in this laboratory (*7*) for the estimation of iodine in foods.

Method

The apparatus is set up and handled exactly as for the estimation of iodine (*7*). It was found, however, that 1 or 2 cc. of nitric acid in each absorber could be substituted for the sodium hydroxide, with equally efficient absorption and the advantage that less acid is required in the later treatment.

After combustion, the water and ash of the cup are transferred to a beaker, the cup and flask rinsed with very dilute nitric acid, and the rinsings added to the beaker together with the contents of the absorption bottles. The combined solutions are evaporated to small volume, then 5 to 20 cc. of sulfuric acid are added, the beaker is covered with a watch glass, and the solution evaporated to fumes. The concentration to small volume before addition of sulfuric acid insures oxidation and expulsion of chlorine, a precaution that is of particular importance in analysis of sea food or other products rich in salt. In a properly conducted combustion there should be no darkening with sulfuric acid, but if darkening does occur, a few drops of nitric acid will clear the solution. From this point the solution or an aliquot of suitable size is treated as provided in the official method.

It was found that while a larger proportion of arsenic than of iodine stays in the combustion chamber, absorption in the washing bottles is not so efficient, so that in some cases the addition of a third washing bottle is desirable. On account of its larger orifice, the Friedrichs wash bottle is very much less efficient than the Milligan in this case, even though the two bottles are alike in principle. Table I gives data from experiments with both types of bottles.

Importance of Oxidation

Usual directions for wet digestion do not stress sufficiently the necessity for constantly maintaining oxidizing conditions. Whenever charring of the sample takes place, arsenic may be reduced from the pentavalent to the trivalent state. According to Rushton and Daniels (*5*) the vapor pressure of arsenious oxide is practically negligible below 250°, and increases to 32 mm. at 275° and 144 mm. at 338° C., the boiling point of sulfuric acid. Appreciable losses might therefore be expected if the digest were heated to vigorous fuming while any reduced material was still present. Analysts generally avoid this danger by keeping the temperature relatively low, with frequent additions of nitric acid, until satisfied that oxidation is complete and arsenic consequently in pentavalent form.

Occasionally substances are encountered which are very difficult to oxidize completely by the wet method, or which contain compounds which interfere with the evolution of arsine in the generator. Fats and oils require long treatment at high temperatures and correspondingly greater amounts of nitric acid. With acid-digested tobacco, Gross (*2*) experienced difficulty which he attributed to the presence of pyridine, and was able to get better recoveries if the arsenic was precipitated by magnesia mixture before marshing, thus separating it from the pyridine. Pyridine is obtained on dry distillation of many proteins, however, and Sörensen and Anderson (*6*) have noted that if nitrogen determinations yield lower values by the Kjeldahl than by the Gunning-Arnold method, the sample contains either ring-like nitrogenous compounds such as pyridine or piperidine which are not decomposed, or substances which yield these compounds on closure of the ring; hence the difficulty encountered by Gross in working with tobacco might occur in many foods rich in protein.

Table I. Distribution of Arsenic in Different Parts of Absorption Train

(10 grams dried shrimp)

	Nitric Acid Used in Absorbers	Sodium Hydroxide Used in Absorbers
	%	%
Combustion chamber	52.83	51.95
1st Friedrichs bottle	4.20	6.43
2nd Milligan bottle	41.69	40.58
3rd Friedrichs bottle	1.28	1.04
	100.00	100.00
	P. p. m.	*P. p. m.*
Total As_2O_3	157.1	154.0

Table II. Recovery of Arsenic from Dried Shrimp

Sample	Weight Taken	As_2O_3 Added	As_2O_3 Found	Recovery of Added As_2O_3	Remarks
	Grams	*Mg.*	*Mg.*	%	
107	10		No stain		Wet oxidation at low temperature
	20		No stain		Wet oxidation at low temperature
	10	1.0	No stain	None	Wet oxidation at low temperature
	10		Trace		Above solution pptd. with magnesia mixture
	20		Trace		Above solution pptd. with magnesia mixture
	10	1.0	1.03	103	Above solution pptd. with magnesia mixture
	10		0.72		Wet oxidation with $CuSO_4$ at high temperature
	10		0.73		Burned in torch
	10		0.725		Burned in torch
	10	1.0	1.69	97	Burned in torch
108	10		0.275		Burned in torch
	10		0.289		Burned in torch
	10		0.288		Wet oxidation with $CuSO_4$ at high temperature
102	10		0.109		Burned in torch
	10	1.0	1.090	98	Burned in torch
	20		0.215		Wet oxidation with $CuSO_4$ at high temperature
113	10		0.048		Burned in torch
	10		0.049		Burned in torch
	10		0.045		Burned in torch
	20		0.097		Wet oxidation with $CuSO_4$ at high temperature
117	10		0.900		Burned in torch
	10		0.980		Burned in torch
	10		0.470		Wet oxidation without $CuSO_4$
	10		0.988		Aliquot of preceding redigested with $CuSO_4$

Application of Torch Method

The authors digested a sample of dried shrimp by the official method, but failed to recover more than traces of arsenic, either with or without precipitation with magnesia mixture. When 1 mg. of arsenic trioxide was added to 10

[1] Associate biochemist, U. S. Bureau of Fisheries.

grams of dried shrimp before digestion, none was recovered by direct marshing of an aliquot, but 1.03 mg. after precipitation with magnesia mixture. The authors concluded that the arsenic of the shrimp was not liberated by the digestion, and that some substance, possibly pyridine, was present in the digest and inhibited the evolution of added arsenic, until removed by separation. This same sample of shrimp, when burned in the torch, yielded duplicate values of 73 and 72.5 parts per million of arsenic trioxide. When digested with acid at higher temperature and with the addition of copper sulfate as a catalyst, as suggested by Maechling (*4*), 72 parts per million were recovered.

A sample of pipe tobacco yielded 17.4 parts per million of arsenic trioxide by wet oxidation, and 24.8 parts after precipitation with magnesia mixture, confirming the observation of Gross. Another sample of tobacco gave 28.0 when treated according to Gross, and 27.4 when burned in the torch. The results shown in Table III indicate that the method can be applied to various kinds of dried vegetable matter.

Table III. Arsenic Recovered from Miscellaneous Foods by Enclosed Torch Combustion

Sample	Description	As_2O_3 Recovered Dry basis	Fresh basis
		P. p. m.	*P. p. m.*
753	Carrot tops	0.34	0.046
1265	Carrot tops	0.16	0.024
856	Cabbage (S. C.)	0.35	0.038
837	Cabbage (S. C.)	0.12	0.008
796	Cabbage (N. Y.)	0.04	0.003
493	String beans (S. C.)	0.32	0.052
794	String beans (Ga.)	0.29	0.025
388	String beans (S. C.)	0.20	0.020
812	Spinach (Va.)	0.59	0.084
857	Spinach (S. C.)	0.94	0.116
A	Dried kelp	88.0	...
B	Dried kelp	97.0	...

The authors also found the torch applicable to the burning of cod liver oil, the oil (usually 5 cc.) being pipetted onto a 6-inch (15-cm.) piece of No. 3 dental cotton roll, the roll enclosed in a segment of Visking sausage casing to prevent loss of oil by contact with the side of the feed tube of the apparatus, and the roll burned. To insure that the roll turns with the feed plate, the bottom of it is split and the two halves are pressed down on the pins of the plate. Twenty samples of American cod liver oil analyzed by this method gave values ranging from 1.9 to 6.7 parts per million of arsenic trioxide (*3*). Duplicate analyses of cotton rolls, to which had been added 10 γ of arsenic dissolved in alcohol, yielded identical results of 10.4 γ. No detectable stain was obtained from the cotton alone.

Conclusion

The method is applicable to products which contain sufficient combustible matter to burn freely in a current of oxygen. Consequently it can hardly have wide application in the estimation of spray residues on vegetables, which would have to be dried and ground before burning, except as a check on acid digestion. Its principal advantages, when applied to dried material or oils, are economy in time and reagents and the elimination of acid fumes from the air of the laboratory. Dry samples ranging in size from 5 to 100 grams can be burned continuously in one operation, at a rate of 1 to 3 grams per minute. The amount of oil that can be burned in one operation is limited to that which a cotton roll will absorb without leaking when subjected to the heat of the torch.

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Determination of Base Exchange in Soils with Copper Nitrate

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The determination of the total base-exchange capacity and the amounts of the various exchangeable bases in soils is important in many soil and agronomic investigations. The results of such determinations have been applied with singular success in the study of morphological and genetical problems pertaining to soils; the study of soil acidity and its related problem, soil liming; the investigation of the availability of plant food cations and their retention when applied as fertilizers; and finally the problem of adequately explaining the development of so-called alkali soils. It is evident that a simple, accurate, and rapid method for the determination of the base-exchange capacity of soils and the amounts of the various exchanged bases should be available to the soil investigator.

By the term "base exchange" is meant the exchange or replacement of the adsorbed cations of the soil by some other cation. Those cations which have been replaced or removed are known as the exchanged or replaced bases. Theoretically any salt can be used to supply the replacing cation, provided it will form an aqueous solution of sufficiently high concentration and be highly ionized. In laboratory practice the soil is usually leached with solutions of one of the following salts: sodium chloride, potassium chloride, ammonium chloride, or ammonium acetate, or with 0.05 *N* hydrochloric acid. Each of these substances as a source of cations has certain inherent objections. When sodium or potassium salts are used as the replacing agents, it is impossible to determine the amounts of these elements in the replaced bases. Another serious objection is that exceedingly small quantities of the replaceable bases, a few milligrams, must be determined in the presence of a high concentration of the replacing agent, usually several grams, or some special method must be used in order to remove these salts, such as volatilization in the case of ammonium salts with possible mechanical losses, or evaporation with nitric acid, which is tedious, disagreeable, and expensive when many determinations are to be carried out, as previously pointed out (*2*). Also it is important to note that all the methods so far proposed and used require for the estimation of

the base-exchange capacity a subsequent replacement from the soil of the adsorbed replacing cation and its quantitative determination in the second leachate. This latter objection is not so serious when the ammonium ion is used as the replacing agent since its quantity can be determined by distillation with magnesium oxide. However, when many determinations are undertaken, this operation requires considerable time and attention.

To eliminate these objections, the authors propose the use of copper nitrate to supply the replacing cation, and the determination of the base-exchange capacity by the electrolytic deposition of copper in the leachate. The electrolytic separation of the copper serves two purposes—namely, the calculation of the base-exchange capacity of the soil and, most important of all, the removal of the replacing cation from the leachate, leaving a solution which can then be used for the determination of the replaced bases, after concentration to small volume to remove excess nitric acid set free during electrolysis.

Method

The method consists in using 250 ml. of approximately 0.3 *N* copper nitrate for leaching 10 grams of soil. The soil is ground to pass a 40-mesh sieve and is then allowed to stand in contact with 125 ml. of the solution for 24 hours. The solution and soil are transferred to a prepared Gooch crucible and leached with the remaining 125 ml. of solution. The soil is then washed with 80 per cent alcohol until the washings are free of copper. This requires about 100 ml. Alcohol is used to wash out the unadsorbed copper ions instead of water, since the latter causes hydrolysis of the adsorption complex with subsequent low values for the base-exchange capacity. The leachate and washings are made up to 500 ml. and an aliquot of this is analyzed for copper and the replaced bases. An aliquot of the original copper nitrate solution is also analyzed for its copper content. The subtraction of the former value from the latter gives the amount of copper adsorbed by the soil, and when expressed in milliequivalents per 100 grams of soil represents the base-exchange capacity of the soil.

For the determination of copper the authors have used with satisfactory results the electrolytic apparatus sold by the Fischer Scientific Company, and also a set-up consisting of storage battery, suitable resistors, ammeter, and voltmeter. The authors have obtained the best results by using 1 to 1.5 amperes and 5 volts. Each determination requires about 45 minutes. Using these conditions, a dense adherent film of copper was obtained which did not flake off through stirring or washing. After removal of the copper the solution was concentrated to convenient volume and the calcium and magnesium were determined by the usual methods.

The authors have also determined the amount of copper ions adsorbed by the soil by replacing these adsorbed copper ions by leaching with 0.1 *M* hydrochloric acid, and electrolytically determining the copper in this leachate.

As a check upon the accuracy of this new method, they have also determined the base-exchange capacity, and the exchangeable calcium and magnesium ions, using the standard neutral ammonium acetate method (*4*). Since the concentrations of replaceable sodium and potassium in the soils reported are exceedingly low, their values were not determined.

Results

In Table I is reported a comparison of the values obtained for base-exchange capacity and for replaceable calcium and magnesium by using the neutral ammonium acetate method and the copper nitrate method upon six soil profiles. Soils 1 to 5, inclusive, are forest soils of the Caddo Series and soil 6 is a Sharkey silty clay loam. The results in all cases are the average of duplicate determinations. It is evident that the two methods yield values which check within the limits of experimental error for base-exchange capacity, and also for the amounts of replaceable calcium and magnesium. The data also show that the amount of copper adsorbed by the soil from the copper nitrate solution can be displaced by hydrogen ions, and that the copper so replaced is equal to the amount of copper lost from the cupric nitrate solution used in the original leaching of the soil.

Table I. Comparison of Base-Exchange Capacity of Six Soil Profiles

	Base-Exchange Capacity[a]			Replaceable[a] Calcium		Replaceable[a] Magnesium	
Soil	Ammonium acetate method	Copper adsorbed by soil	Copper recovered from soil	Ammonium acetate method	Copper nitrate method	Ammonium acetate method	Copper nitrate method
1A	7.58	7.45	7.23	4.68	4.46	2.24	2.52
1B	9.91	10.68	10.61	5.45	5.18	1.75	1.48
1C	32.75	32.70	32.60	23.20	23.85	3.23	3.50
$2A_1$	12.36	12.57	12.44	4.55	4.46	2.11	2.57
$2A_2$	3.43	3.46	3.45	3.21	3.21	1.16	1.07
2B	8.69	8.33	8.22	7.31	7.31	2.61	2.55
2C	21.45	21.40	20.90	15.95	16.55	3.27	3.59
3A	2.22	2.51	2.23	2.31	2.14	Trace	Trace
3B	12.80	12.73	12.84	6.51	6.86	3.41	3.19
3C	15.70	15.87	15.88	10.17	10.67	3.24	3.32
4A	5.92	6.29	6.30	4.61	4.91	Trace	Trace
4B	19.50	19.50	18.92	14.59	14.25	1.86	1.62
4C	14.51	13.89	13.90	12.17	12.11	0.96	0.97
5A	5.70	5.97	6.02	3.56	3.72	1.07	1.03
5B	9.70	9.28	9.14	6.05	6.21	1.65	1.73
5C	14.90	14.45	14.26	10.25	10.38	2.11	2.29
6A	24.01	24.05	24.01	16.30	16.50	2.33	2.38
6B	11.19	11.16	11.08	9.26	9.10	1.61	1.69
6C	36.10	35.75	35.72	19.26	19.36	2.82	2.82

[a] Milliequivalents per 100 grams of soil.

Previously it was generally agreed that base exchange in soils could be represented by stoichiometrical relationships, but later work has shown that within narrow limits it is a function of the hydroxide-ion concentration of the replacing solution, and also that these cannot be differentiated from the exchangeable cation (*1*, *3*). The results reported here, while not offering conclusive proof, indicate very clearly that stoichiometrical relationships do hold for base exchange in soils.

Conclusions

A rapid and accurate method for the determination of the base-exchange capacity of soils is proposed, which results in considerable saving in time when compared to the standard ammonium acetate method and eliminates some objections which have been raised to the older methods.

A 0.3 *N* solution of copper nitrate is used to replace the adsorbed bases, the decrease in copper content of replacing solution being used as a measure of the total exchange capacity of the soil. The removal of the copper from the leachate by electrolysis results in a solution which can be used, after evaporation to small volume to remove the excess nitric acid, for the determination of the replaced bases.

If desired, a check upon the accuracy of the base-exchange capacity can be obtained by leaching the adsorbed copper from the soil by means of dilute hydrochloric acid and estimating the amount of copper in this leachate by electrolysis. The replacement of the adsorbed bases of soils by copper ions is quantitative and can be represented by stoichiometrical values.

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Determination of Citrate

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A relatively simple procedure is presented for estimating citrate in a solution containing as little as 1 mg. in a 5-ml. sample. The procedure consists principally in oxidizing citric acid by means of potassium permanganate in the presence of mercuric sulfate. The insoluble precipitate formed is determined gravimetrically. The analysis may be completed in 3 to 4 hours. A study of the conditions required in the determination and of some possible sources of interference is made.

For investigations requiring large numbers of citrate determinations, such as the study of decomposition of citrates by microörganisms, a relatively simple and rapid method for estimating citrate is desirable. The most general methods available for the determination of citric acid are: (*a*) acetone formation (*1, 6, 15*); (*b*) pentabromoacetone formation (*5, 8, 9, 11, 12*); (*c*) mercuric sulfate complex formation (*2, 4, 13, 14*); (*d*) enzymatic dehydrogenation (*12*); and (*e*) esterification (*10*). These methods have their peculiar limitations, some in the large quantity of material required for a determination or the excessive time necessary for complete analysis; some in the appreciable volatility and solubility of the analytical precipitate, the limited number of concurrent determinations feasible, the delicate control needed, or the complicated apparatus demanded.

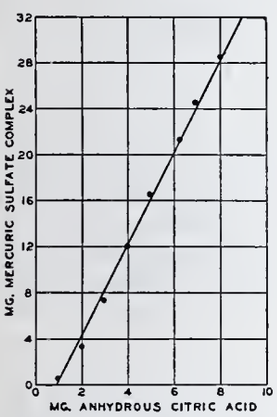

Figure 1. Relation between Citric Acid and Mercuric Sulfate Complex

The mercuric sulfate method was selected for its rapidity and convenience. A detailed study of some of its limitations, including the effect of temperature, acidity, and rate of oxidation on the amount of mercuric complex produced, was made. It was found that control of volume during oxidation and the use of centrifuge tubes rather than Gooch crucibles increase accuracy and speed. Interference from aconitic acid has been established, but moderate amounts of formate, acetate, succinate, malate, tartrate, lactate, and phosphate do not interfere.

Experimental Procedure

The method consists in precipitating citric acid with barium acetate in dilute alcoholic solution to separate it from interfering substances. The precipitated citrate, which is soluble in acid, is then oxidized by permanganate in the presence of mercuric sulfate, yielding a very insoluble precipitate. This is determined gravimetrically and compared with the weight of a precipitate formed from known amounts of citrate treated in the same way.

Materials and Apparatus. The following solutions are prepared:

1. A fresh solution of analyzed anhydrous citric acid (*3*) containing 2 mg. of citric acid per ml.
2. Ten per cent barium acetate.
3. Saturated barium hydroxide.
4. Fifty per cent alcohol with one per cent barium acetate.
5. Eighty-five per cent phosphoric acid.
6. A solution of mercuric sulfate, made by dissolving a suspension of 50 grams of mercuric oxide in 500 ml. of water by the gradual addition of 200 ml. of 96 per cent sulfuric acid and diluting to 1000 ml.
7. One per cent potassium permanganate.
8. Fifty per cent alcohol.

Heavy-walled Pyrex glass centrifuge tubes of 15 ml. capacity, numbered, weighed, and marked at 10 ml. are used. A copper stand holds the centrifuge tubes in a water bath and a special stirrer is used when permanganate is added to each in turn. The stirrer is made from a 25-cm. length of 3-mm. glass rod, fitted with a glass bearing and rubber stopper as holder. The upper end is bent to a small hook and weighted. The lower end is bent to a short spiral small enough to enter the centrifuge tubes, with a 2-cm. tip to prevent the stirrer from sticking in the cone. This stirrer when mounted is operated by a string in the hand of the analyst. Graduated 1-ml. pipets are used to measure the mercuric sulfate and phosphoric acid solutions. Potassium permanganate is added from a 10-ml. buret having a rubber connection with a glass pearl and a bent tip. This type of buret permits more accurate control of the rate of addition of the reagent than the type with a glass stopcock. A silver or platinum wire is used for stirring the precipitate in the wash liquid.

Procedure. For known quantities of citric acid, six centrifuge tubes containing 1 to 5 ml. of the standard solution are a convenient series. To each is added 1 ml. of 10 per cent barium acetate and four drops of saturated barium hydroxide. The precipitation of the barium salt is completed by the addition of two volumes of 95 per cent alcohol. After standing 10 minutes, the precipitate is centrifuged for 5 minutes and is washed three times by centrifuging with 3 ml. of 50 per cent alcohol containing 1 per cent barium acetate. After the precipitate is well drained (10 minutes at 30° C.), it is dissolved in a mixture of 3 ml. of water and 0.16 ml. of phosphoric acid. For 5 minutes this solution is placed in a boiling water bath to insure complete elimination of the alcohol.

To the hot solution is added 1 ml. of the mercuric sulfate reagent. After the precipitate has settled, the solution is diluted with water to 10 ml., centrifuged, and decanted through a filter into a small beaker. Eight ml. of the filtrate are transferred to a weighed 15-ml. centrifuge tube, and 0.2 ml. of mercuric sulfate reagent and 1 ml. of water are added. The tube is placed for 1 minute in a water bath at 85° C., a drop of 3 per cent hydrogen peroxide is added, and with continuous stirring, 1 per cent potassium permanganate is added at a rate not exceeding one drop in 10 seconds until a faint pink color persists for 10 seconds. One drop of hydrogen peroxide is added. After 1 minute the stirrer is rinsed off, and the tube cooled and centrifuged for 5 minutes. Upon decanting the supernatant liquid, the precipitate is stirred with 3 ml. of 50 per cent alcohol and centrifuged again. Washing is repeated three times. During the process a slight scum occasionally escapes from precipitation; but the combined scum from eight such tubes weighs less than 0.2 mg. After draining for 5 minutes, the tube is wiped off and dried at 100° C. for an hour, or in a vacuum oven for half an hour. No change in weight occurs on standing overnight. The weights of precipitate, multiplied by 10/8 to correct for the fraction of the original solution taken, when plotted against the known amounts of citric acid, form a straight line between 1 and 10 mg. of acid (Figure 1).

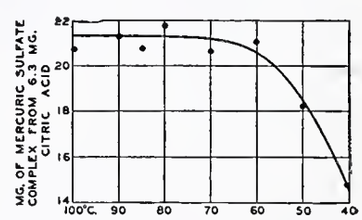

Figure 2. Effect of Temperature on Yield of Mercuric Sulfate Complex

The same procedure applies to the determination of citrate in some mixtures of organic materials. Certain precautions

are necessary in this case, however, and these are discussed after some sources of error are considered.

Studies of Interference

By the precipitation of the barium salt, interference due to chloride ions has been avoided. Phosphate has not been found detrimental. Although Gowing-Scopes (*4*) has reported that the precipitate is dissolved by prolonged exposure to hydrogen peroxide, no interference from this source has

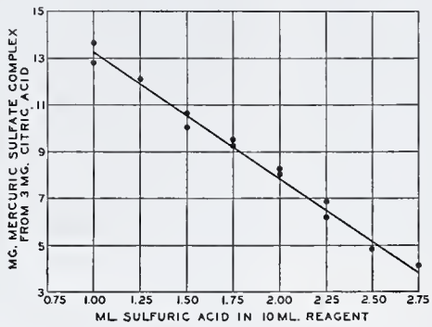

Figure 3. Effect of Acid Concentration on Yield of Mercuric Sulfate Complex

been found in the present procedure. The small amount of peroxide introduced does not alter the weight of precipitate appreciably until the period of contact is many times that given in the procedure.

Studies on the effect of formate, acetate, and succinate on the amount of mercuric sulfate complex formed are summarized in Table I. No interference was observed.

Table I. Absence of Interference by Succinate, Acetate, and Formate

	Mercuric Sulfate Complex
	Mg.
8.0 mg. anhydrous citric acid	29.1
+ 2 mg. sodium succinate	29.0, 28.2
+ 2 mg. each of sodium acetate and succinate	29.1, 28.3
+ 2 mg. each of sodium formate, acetate, and succinate	28.6, 28.7

While U. S. P. lactic acid yielded a rather large precipitate with this procedure, distilled lactic acid and pure zinc lactate did not. A study of the influence of tartaric and malic acids on the yield of the precipitate from citric acid showed that no appreciable error was introduced within the range selected. The results of these studies are summarized in Table II. The maximum error is equivalent to about 0.4 mg. citric acid.

Table II. Effect of Tartaric and Malic Acids on Citrate Determination

Anhydrous Citric Acid	Mercuric Sulfate Complex	Tartaric Acid Added	Mercuric Sulfate Complex	Malic Acid Added	Merucric Sulfate Complex
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1.9	2.9	3.0	3.4	3.0	3.3
5.0	16.5	3.0	16.4	3.0	16.5
8.1	28.7	3.0	30.4	3.0	29.9

Of the various substances studied, only one has been found to offer serious interference. This is aconitic acid, which is closely related in structure to citric acid. This material, whether used as a commercial c. p. chemical, or whether further purified, yielded a precipitate when subjected to the same procedure as citric acid. (See Table III.)

Table III. Mercuric Complex Obtained from Aconitic Acid

c. p. Aconitic Acid (d. 192°)	Mercuric Sulfate Complex	Recrystallized Aconitic Acid (Water)	Mercuric Sulfate Complex
Mg.	*Mg.*	*Mg.*	*Mg.*
8.5	5.9	7.9	5.9
7.0	5.6	5.9	4.0

Effect of Temperature

Since the product of oxidation in this procedure is presumably acetone dicarboxylic acid, the objection may be raised that the known instability of this acid at elevated temperatures may cause erratic deviation in the results. Since this acid may be kept for months at 7° C. but is almost instantly decomposed at 100°, the rate of decomposition evidently varies with the temperature. The yield of mercuric sulfate complex might therefore increase as the temperature is lowered from 100°. Experimental study has shown that this is not the case. The amount of precipitate remained practically constant between 70° and 100°, and therefore no error due to changes in temperature will be encountered when the temperature is kept above 70° C. Below 70° the amount of precipitate decreases (Figure 2). An explanation for this may be found partly in the observation of Kuyper (*7*) that oxidation of citric acid is more complete at lower temperatures, and partly in the fact that, while oxidation and complex formation occur practically instantaneously at elevated temperatures, the rate becomes slower at the lower temperatures, and the easily oxidized product is subjected to further oxidation before it is removed as an insoluble precipitate.

Effect of Acidity

The effect of varying the acid concentration in the oxidation has been studied by changing the amount of sulfuric acid added with the mercuric sulfate reagent. Various amounts of sulfuric acid were added with stirring to 0.5 gram of mercuric oxide suspended in 10 ml. of water. The limits between which this variation may be studied are on the one hand the lowest acidity which suffices to prevent spontaneous hydrolysis of the reagent in the hot solution before oxidation, and on the other hand, the highest acidity at which the reagent may be held in solution. The former was found to lie between 0.75 and 1.00 ml. and the latter at about 2.75 ml. The yield of mercuric sulfate complex decreased linearly with increasing amounts of sulfuric acid (Figure 3).

The sensitivity of the determination can be increased by diminishing the acid concentration between the limits indicated. The reagent made by using 1.0 ml. of sulfuric acid permits detection of half as much citrate as can be found by the usual method using 2.0 ml. This may be of particular importance where small amounts of material are to be analyzed.

Discussion of Results

The method for analysis of citric acid by the mercuric sulfate procedure as modified here can be used for samples containing 1 to 10 mg. of citric acid in 1 to 5 ml. of solution. By using half the amount of sulfuric acid in the reagent, as little as 0.1 mg. per ml. can be found. This modification has not seemed desirable for larger quantities because the precipitate assumes a dark appearance during the extended period of oxidation.

The volume of the solution from which the barium salts are precipitated does not materially influence the result within the indicated limits. The results of Täufel and Mayr (*15*) show that, in the presence of an excess of the precipitating agent, the solubility of barium citrate in 50 per cent alcohol is sufficiently low to allow an accuracy of 0.1 per cent.

No interference was encountered from formic, acetic, succinic, malic, lactic, or tartaric acids in amounts comparable with the citric acid present. Where much larger amounts of substances precipitable by barium acetate are present, it is necessary to use larger amounts of the reagent. To test this possibility, the supernatant fluid from the pre-

cipitation of an unknown mixture of barium salts should be treated with more reagent before it is discarded. It is necessary to neutralize the sample if much strong acid is present, since the precipitation of the barium salt is most complete in a neutral or slightly alkaline medium.

Interference by aconitic acid requires a qualitative test for the absence of this material in the unknown mixture in order to determine the applicability of the method. The pink or blue coloration of acetic anhydride at 100° C. (*16*) is of some value in detecting aconitic acid. The absence of this coloration indicates absence of aconitic acid.

The rate of oxidation should be not greater than one drop of potassium permanganate solution in 10 seconds, since more rapid oxidation gives low results. The use of other oxidizing agents or more dilute permanganate was not found advantageous in the present procedure. For the smaller quantities in particular, the addition of manganous sulfate has proved useful, but this has not been essential for the successful application of the method within the sample range considered here. All the oxidative methods apply to the citrate ion; trimethyl citrate and citric triamide, for example, give no evidence of citrate content by the permanganate procedures unless they are first hydrolyzed.

Acknowledgment

Acknowledgment is made of the helpful criticism of M. Kunitz and the technical assistance of B. Prytz.

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A Large-Size Modified Soxhlet for Hot Extractions

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The need for a modified Soxhlet extractor intermediate between the large-size Soxhlets ordinarily used for quantitative determinations and the very large extractors described by Cameron (*1*), Drake and Spies (*2*), and McCay (*4*) but more refined than that described by Liston and Dehn (*3*) led the authors to design the extractor shown in Figure 1. This extractor is especially useful where the material is fibrous in structure or is to be given a hot extraction.

The apparatus consists of three parts like the ordinary Soxhlet: the condenser *A*, the extractor body, *C*, and the receiving flask which fits at *D*. Condenser *A* consists of a 12-inch (30-cm.) Allihn condenser having the delivery tube bent and cut as shown. The flask (not shown) is a 2-liter flat-bottom flask having a No. 30 standard taper joint to fit at *D*. The body of the extractor, *C*, is 16 inches (40 cm.) in length (over-all) and carries a No. 50 standard taper joint, *B*, at the top and a No. 30 standard taper joint, *D*, at the bottom. The vapor tube, *G*, having a vent, *V*, at the top, carries the siphon tube *E*, fastened at points *H* to give it strength and protected by the shield, *F*. *F* is vented at *I* and carries 6 or 8 holes, *J*, at the bottom. The body is 5 inches (12.5 cm.) in diameter and 10.5 inches (26 cm.) in height (exclusive of joints). Shield *F* is 2 inches (5 cm.) in diameter. The volume of liquid required to cause siphoning (extractor empty) is 1900 cc.

This extractor overcomes the chief difficulty found in most Soxhlets—imperfect siphoning—by the use of the large siphon shield *F*. This shield, besides protecting the siphon tube, acts as a reservoir so that the siphon is always in contact with liquid, the reservoir being so large that the solvent has considerable time to drain from the sample into the reservoir before the reservoir is emptied. For best results siphon tube *E* should be flattened at the top and constricted at the bottom as advised by Cameron (*1*).

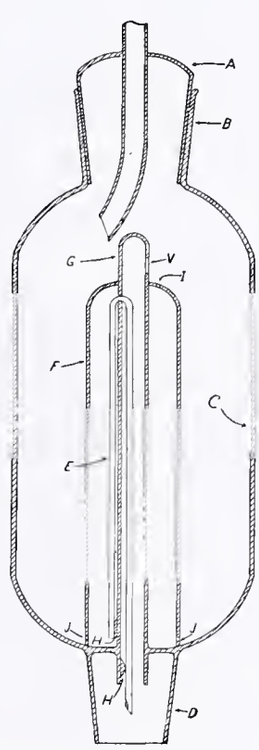

Figure 1

The fact that the vapor tube, *G*, passes through the liquid in the extractor means that only constant-boiling solvents, or those which have a very short boiling range, may be used because the liquid in the reservoir is always hot and refluxing will occur to such an extent that no extraction will take place if the solvent has a wide boiling range. However, by placing a chimney around the body of the extractor in such a manner that little heat is lost by radiation, extraction at a few degrees below the boiling point of the solvent will take place when a constant-boiling solvent is used. Since siphoning is clean and rapid, very good hot extractions can be carried out in this manner. If low-boiling solvents are used and exceptionally rapid extractions are desired, it would no doubt be advantageous to replace condenser *A* by one of the type described by Cameron (*1*).

The extractor described above has been used mainly for the alcohol extraction of cotton linters, although other solvents have been employed. With this solvent excellent results have been obtained over a period of 6 months.

Acknowledgment

The authors wish to acknowledge the assistance of Otto Greiner & Company, of Newark, N. J., who made this extractor from Pyrex glass to specifications.

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Determination of Butter Fat in the Presence of Coconut Oil

A Modified Kirschner Procedure

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THE regular Kirschner test[1] for the determination of butter fat in the presence of coconut oil has a number of inherent disadvantages which limit its usefulness. It calls for a second distillation of the fatty acids and depends upon the use of silver sulfate, which is not very soluble or quick in its action.

The modification to be described reverses the regular procedure in that it avoids the second distillation and operates directly upon that portion of the fatty acids precipitated by silver. Also, the use of silver nitrate as the silver salt insures quick and clean precipitation. This process has been in use for many years in this laboratory in controlling the composition of oleomargarine which contained 10 per cent of butter fat and a similar amount of coconut oil. The authors' modification of this method (called the Kirschner-Flanders procedure) is as follows:

Modified Method

The Reichert-Meissl determination is carried out as usual, using glycerol soda for the saponification. The distillation is best conducted on an electric heater capable of close regulation, as the time of distilling 110 cc. must be 30 ± 0.5 minutes for good results.

The 110 cc. of distillate are titrated in a 300-cc. Erlenmeyer flask with 0.1 N sodium hydroxide, using phenolphthalein indicator and running to a distinct end point. This gives the Reichert-Meissl number, which should be corrected by a blank titration found by carrying through the heating and distillation on the glycerol soda solution alone.

Add 5 cc. of 10 per cent silver nitrate solution to the neutralized Reichert-Meissl distillate. Let it stand 30 minutes with occasional rotatory shaking. (The flask should be stoppered.) Filter on a 9-cm. paper (Whatman No. 41). Let filter drain (do not wash precipitate). Transfer precipitate to a separatory funnel with cold water and also rinse out flask into separatory, using as little water as possible. Rinse flask with 15 cc. of 0.1 N sulfuric acid and pour the acid over the filter, into the separatory. Rinse filter with a little water and discard paper.

Stopper the separatory and shake vigorously till precipitate is dissolved. Rinse the flask with 15 cc. of chloroform and add to separatory. Shake well and let stand until the chloroform clears. Draw chloroform layer carefully through a dry filter (Whatman No. 4) into a 150-cc. Erlenmeyer flask. Repeat extraction twice with 10-cc. portions of chloroform, letting stand a few minutes each time before drawing off. Rinse filter with 25 cc. of additional chloroform. Add 3 or 4 drops of phenolphthalein indicator made up with absolute alcohol. Titrate directly in chloroform with 0.1 N sodium ethylate solution to strong end point.

The titration is carried out in the absence of water. The standard sodium ethylate is prepared from cleaned sodium and absolute alcohol and may be standardized in the usual way against standard hydrochloric acid. The chloroform used must be washed, if not neutral, and filtered through dry paper to remove water.

For practical use the figures as shown in Table I should be plotted on plain cross-section paper, with increasing percentages running vertically and titrations horizontally. The Reichert-Meissl value of the pure butter fat is taken as 28 and is drawn as a straight line. The Kirschner-Flanders and Reichert-Meissl values yield curves of similar shape. The proportion of the volatile acids precipitated by silver varies from 81 per cent at 10 per cent coconut oil in the mixture to 76 per cent when pure coconut oil is used.

[1] Assoc. Official Agr. Chem., Methods of Analysis, 3rd ed., p. 324 (1930).

The authors' experience with this method has been principally on oleomargarine containing 10 per cent of butter fat and from 6 to 15 per cent of coconut oil. Under these conditions it has given results very close to the true value for butter fat and approximate values for the coconut oil. In this range fairly close results for the butter fat may be secured on mixtures of butter fat with coconut oil by subtracting the Kirschner-Flanders titration from the Reichert-Meissl and dividing the result by 28.

Table I. Pure Butter Fat and Coconut Oil Alone

	Butter Fat		Coconut Oil	
	Reichert-Meissl	Kirschner-Flanders	Reichert-Meissl	Kirschner-Flanders
%				
100	28.0	4.0	7.8	6.0
90	..	3.5	7.6	5.85
80	..	3.0	7.2	5.6
70	..	2.5	6.85	5.4
60	..	2.05	6.4	5.1
50	..	1.6	6.0	4.8
40	..	1.2	5.5	4.5
30	..	0.8	4.8	4.0
20	..	0.5	3.9	3.2
10	..	0.25	2.7	2.1
5	..	0.1	1.8	0.8

Table II. Results with Varying Amounts of Butter Fat and Coconut Oil

Fat Mixture						
Butter fat	Coconut oil	Reichert-Meissl[a]	Kirschner-Flanders[a]	Kirschner[a]	Butter Fat by Kirschner	Butter Fat by Kirschner-Flanders
%	%				%	%
50	50	17.7	5.6	12.6	55.4	48.6
40	40	15.1	5.2	10.1	44.7	39.7
30	30	11.6	4.2	7.6	33.6	29.3
20	20	8.4	3.2	5.0	22.1	20.7
15	15	6.3	2.6	3.7	16.4	14.6
10	10	4.8	2.0	2.5	11.7	10.9
5	5	2.7	1.0	1.2	5.3	6.6
80	20	23.6	5.8	19.7	87.1	73.2

[a] Cc. 0.1 N sodium hydroxide.

When larger percentages of butter fat are involved more exact results may be secured by the following formula:

$$\% \text{ butter fat} = \frac{(A - B) + C \times 100}{28}$$

where A = Reichert-Meissl value
B = Kirschner-Flanders value
C = correction for part of Kirschner-Flanders due to butter fat

Using $A - B$ as an approximation for the Reichert-Meissl value of the butter fat present we find the corresponding Kirschner-Flanders value for pure butter fat on the Reichert-Meissl and Kirschner-Flanders curves, which can be plotted from Table I.

For example, a mixture containing butter fat and coconut oil had a Reichert-Meissl value of 17.7 cc. and a Kirschner-Flanders value of 5.6 cc.: $A - B = 12.1$. Using this approximation of the R. M. value for the butter fat present we find by running up to the R. M. line a corresponding K. F. value of 1.3. Adding this to 12.1 we get 13.4. By using this corrected value and again referring to the R. M. line we find it would have a K. F. of 0.2 higher, or 1.5. This is the value C, or the true K. F. value corresponding to the butter fat present. Adding this to $A - B$ or 12.1, we get 13.6, which divided by 28 and multiplied by 100 gives 48.6 per cent.

By subtracting the K. F. number from the total R. M. value we have taken off not only that portion of the acids from coconut

oil which were precipitated by silver, but also those from butter fat. This is not serious when the percentage of butter fat is in the neighborhood of 10 per cent, but becomes serious when larger percentages are present. By means of the approximate value $A - B$, we may determine what the K. F. was and add it as a correction.

Table II gives results obtained on several samples containing varying amounts of butter fat and coconut oil. Results by the regular Kirschner method are given for comparison, also the percentages of butter fat indicated by dividing these results by the average factor 22.6.

A very interesting set of curves showing the relation between the Reichert-Meissl, Kirschner-Flanders, and Kirschner values may be secured by plotting all the values given in both tables on the same sheet of cross-section paper.

A consideration of the curves obtained would indicate that the method should be most useful on mixtures containing up to 30 per cent of butter fat and from 10 to 40 per cent of coconut oil. The lower range might be extended by the addition of just enough of the silver salt of the fatty acids to saturate the solution in which the precipitation is to be made. On the Kirschner-Flanders curve this would appear to be the equivalent of 5 per cent of coconut oil. This the authors have never tried, but offer the suggestion for what it is worth.

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Columbium in Steel

Determination in 18-8 Chromium-Nickel Steel and in Low-Titanium Steel

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The use of columbium in steel is increasing rapidly, and a simple gravimetric method for its determination in alloy steels is available. Weiss and Landecker (*2*), in a summary of the properties of columbium and tantalum, stated that they could be separated from solution by perchloric acid, quantitatively, and in an easily filterable form. It was found that fuming with perchloric acid also gave an easily filterable product.

Procedure

Columbium. Two grams of alloy steel (0.8 per cent columbium, 18 per cent chromium, 9 per cent nickel) were dissolved in about 25 cc. of dissolving solution (750 cc. hydrochloric acid, 250 cc. nitric acid, 1000 cc. water) in a 400-cc. beaker. After the steel had been completely disintegrated, 20 to 25 cc. of 70 per cent (technical) perchloric acid were added; the heating was continued until red chromic acid formed and then 5 minutes longer. The contents of the beaker were cooled and diluted to 100 cc. with water, the chlorine was boiled out, and the precipitate was filtered off on a No. 40 Whatman paper.

The paper was washed six times with hydrochloric acid (1 to 10) and once with water to remove excess acid. The paper was transferred to a tared platinum crucible, the paper charred, and the crucible ignited, cooled, and weighed. This gave columbium pentoxide plus silica. About 5 cc. of 1 to 5 sulfuric acid and 3 to 4 drops of hydrofluoric acid were added. The crucible was heated (150° to 200° C.) to fumes of sulfuric acid, and then till practically all acid had been evaporated. The upper edge of the crucible was heated in the flame of a Meeker burner (because of danger of spitting), and increasing portions of the crucible were ignited to drive off more acid; finally the residue in the crucible was heated to about 900° C. to drive out the last traces of acid. Columbium pentoxide remained. Silica was obtained by difference.

The residue on the filter paper was black, which might indicate lower oxides or the carbide of columbium. To determine carbon, a sample of steel was fumed in perchloric acid, filtered off on a small Gooch crucible, and washed with hydrochloric acid and then with water. The crucible was dried at 110° C. and placed in a carbon furnace apparatus; the carbon was determined and found to be 0.05 per cent. It is possible that lower oxides of columbium were present. Hydrofluoric acid changes the residue to the higher oxide of columbium.

Redigestion of the black precipitate on the paper with a mixture of nitric and perchloric acids is of no help. However, if hydrofluoric acid is added to the original dissolving solution, the residue from the perchloric acid treatment will be light yellow but will contain some silica. Such treatment of the steel would have no advantages.

In the removal of the silica by hydrofluoric acid, sulfuric or nitric acids may be used, but in decided excess to prevent partial volatilization of columbium as the fluoride. The residue must be ignited strongly to remove the last traces of the acid radical present. The oxide is yellow when hot and nearly white when cold. The oxide may easily be removed from the crucible by fusion with phosphate.

If the steel is dissolved in hydrochloric acid (1 to 2), cooled, and cupferron added, columbium, some iron, silica, and carbides are found on the filter paper. When the paper is returned to the beaker, treated with 10 cc. of nitric plus 10 cc. of perchloric acid, fumed, and then treated as in the usual procedure, all the columbium will be found in the residue.

Titanium. It has been shown (*1*) that titanium originally present in a steel sample can be dissolved out with perchloric acid. Weiss and Landecker (*2*) found that titanium causes tantalum and columbium to react differently after fusion than if titanium were absent. A steel containing both columbium and titanium was not available. However, a 1-gram sample containing columbium and a 1-gram sample containing 0.30 per cent titanium were mixed and run for columbium. The residue indicated that the perchloric acid had taken up all the titanium, and left the columbium. It has been found that perchloric acid will hold at least 12 mg. of titanium in solution.

Tantalum. Tantalum is expected to react in the same manner as columbium but no samples of tantalum in steel have been received.

The data obtained are as follows:

	1 g. Steel Treated with HNO_3–HF in Pt Crucible		2 g. Steel Treated with HF–H_2SO_4 by Cupferron Method
Crucible, SiO_2, Cb oxide, grams	19.8545	19.8443	25.0994
Same, after HF treatment, grams	19.8441	19.8341	25.0958
Crucible, grams	19.8318	19.8219	25.0715
SiO_2–Cb_2O_5, gram	0.0227	0.0224	
SiO_2, gram	0.0104	0.0102	
Cb_2O_5, gram	0.0123	0.0122	0.0243 (2 g.) 0.0122 (1 g.)
Si, %	0.49	0.48	...
Cb, %	0.86	0.85	0.85

	1 g. Cb + 1 g. Ti (0.30%) Steels Mixed		C in a 2-g. Residue
Crucible + oxides, grams	16.0461	2 g. CO_2, gram	0.0038
Same, after HF treatment, grams	16.0264	1 g. CO_2, gram	0.0019
Crucible, grams	16.0143	Carbon, %	0.05
Remainder, gram (shows no Ti)	0.0121		

Literature Cited

(1) Silverman, Louis, *Chemist-Analyst*, **23** (July, 1934).
(2) Weiss and Landecker, *Chem. News*, **101**, 2, 13, 25 (1910).

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Determination of Malic Acid in Plant Tissue

Simultaneous Determination of Citric and Malic Acids

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Malic acid, when oxidized by potassium permanganate in the presence of potassium bromide, is converted into a bromine compound that is volatile with steam. This substance combines with dinitrophenylhydrazine in acid solution to yield a product insoluble in water which can be filtered off and dissolved in pyridine. The pyridine solution, when diluted with water and made alkaline with sodium hydroxide, promptly develops a blue color suitable for spectrophotometric measurements, strictly proportional to the quantity of malic acid taken over the range 0.1 to 2.5 mg., and stable for several hours. The same product is formed from both optically active and inactive malic acid.

A method, based upon this reaction, has been developed to determine the malic acid content of dried leaf tissue, or of extracts from leaves, and has been applied to tobacco leaf. Preliminary experiments have shown that it can readily be adapted to the investigation of the malic acid content of muscle, blood, and urine, and also to the determination of aspartic acid after this has been deaminized with nitrous acid.

Malic acid is one of the most widely distributed organic acids found in plants, and frequently occurs in relatively high concentration in them. A method for its accurate determination is therefore a matter of considerable importance in plant physiology; unfortunately, however, none of the methods that have been proposed hitherto are suitable for the estimation of small quantities.

Methods that depend upon precipitation of the acids as lead or barium salts (*4*, *5*, *9*), with subsequent preparation and fractional distillation of the esters, can be successfully applied only to large quantities of material. The method most commonly used in recent years is based upon the high optical rotation of malic acid in the presence of uranium (*2*) or of molybdenum (*1*) salts. This method is specific only in the absence of other optically active acids; furthermore, the possibility that *dl*-malic acid may sometimes be present in plant tissues (*8*) introduces an element of uncertainty into the result as a measurement of the total quantity of malic acid present.

The method described in the present paper depends on the observation that malic acid, when treated with potassium permanganate in the presence of potassium bromide under the proper conditions, is converted into a bromine compound that is volatile with steam. This substance yields an extremely insoluble condensation product when heated with dinitrophenylhydrazine in acid solution. The ratio between the amount of this product and of the malic acid submitted to oxidation is constant, and the quantity can be easily estimated by dissolving the product in pyridine, diluting with water, and making the solution alkaline with sodium hydroxide. The intense blue color formed is in every way suitable for measurement in a Pulfrich spectrophotometer.

The specificity of this reaction with respect to the common organic acids is remarkable. A quantity of 0.2 mg. of malic acid gave a distinct orange precipitate after heating the oxidation product with an acid solution of dinitrophenylhydrazine, but 25 mg. each of acetic, lactic, fumaric, succinic, pyruvic, tartaric, maleic, glycollic, and glyoxylic acids failed to give any precipitation when oxidized and treated in the same way. Citric acid is converted into pentabromoacetone by the oxidation procedure employed, and this substance yields a precipitate with dinitrophenylhydrazine. No difficulty is thereby presented, however, since pentabromoacetone, if present, is readily removed from the oxidation mixture by extraction with petroleum ether. This solvent does not extract the oxidation product of malic acid.

Products that yield precipitates with dinitrophenylhydrazine are formed when carbohydrates or certain amino acids are subjected to oxidation with potassium permanganate. But no such compound is formed from either malic or citric acid, unless potassium bromide is also present during the oxidation; consequently it is possible to estimate malic acid in the presence of these interfering substances if two parallel oxidations are conducted, one with and one without bromide, and the resulting solutions are extracted with petroleum ether to remove pentabromoacetone. The difference in the yields of dinitrophenylhydrazine derivative then represents with considerable accuracy the quantity of malic acid present, inasmuch as the bromide has no effect upon the oxidation of the carbohydrates. It is generally more convenient, however, to eliminate the amino acids and carbohydrates as a preliminary step by extracting the organic acids with ether from the material under investigation.

Although considerable study has been given to the nature of the oxidation product of malic acid, a detailed explanation of the chemical reactions that occur has not yet been obtained. It seems better therefore at present to describe the reaction from an entirely empirical point of view.

Reagents

Sulfuric acid, 50 per cent: a mixture of equal volumes of concentrated acid and water.

Potassium bromide, 1 *M*: 11.9 grams diluted to 100 cc.

Potassium permanganate, 1.5 *N*: 47.4 grams diluted to 1000 cc.

Bromine water: saturated aqueous solution.

Sulfuric acid, 2 *N*: 28 cc. of concentrated acid diluted to 500 cc.

Hydrogen peroxide, 3 per cent: ordinary commercial product.

Petroleum ether: boiling point, 35° to 50° C.

Sodium sulfide, 4 per cent: 4 grams of crystalline sodium sulfide diluted to 100 cc., prepared fresh every 2 to 3 days.

Hydrogen peroxide (halogen-free): 4 grams of sodium peroxide dissolved in 50 cc. of water, cooled, and faintly acidified to Congo red with 50 per cent sulfuric acid (7 to 8 cc. required); prepared fresh every week.

Silver nitrate, 0.02604 *N*: 4.4231 grams of pure silver nitrate diluted to 1000 cc. 1 cc. = 1.0 mg. of citric acid.

Ammonium thiocyanate, 0.02604 *N*; 1.98 grams diluted to 1000 cc. and standardized against the silver nitrate.

Ferric ammonium sulfate (ferric alum): 30 grams dissolved by warming with 100 cc. of water.

Dinitrophenylhydrazine: 5 grams of Eastman's dinitrophenylhydrazine are ground in a mortar with several successive portions of a mixture of 200 cc. of concentrated hydrochloric acid with 800 cc. of water. The whole is then transferred to a beaker and boiled for 1 to 2 minutes with vigorous stirring; after being cooled, the solution is diluted to 1000 cc. with water and filtered through hard paper. The reagent is filtered again just before using.

Sodium sulfite, 20 per cent: 20 grams of crystalline sodium sulfite diluted to 100 cc., prepared fresh every 2 to 3 days.

Pyridine: Eastman's pyridine (pract.) is redistilled.

Sodium hydroxide, 5.0 *N*: 200 grams of C. P. sodium hydroxide diluted to 1000 cc.

Preparation of Organic Acid Fraction

Two grams of the dried and powdered tissue are acidified to pH 1 with sulfuric acid, mixed with 3.5 grams of asbestos, and extracted with ether according to the technic of Pucher, Vickery, and Wakeman (*7*). The organic acids are transferred to aqueous alkali and the solution is made to 100 cc. If extracts of tissue are employed, a portion equivalent to 2 grams of the tissue is evaporated to a sirup (not to dryness), acidified to pH 1 with sulfuric acid, and mixed with the asbestos; the mixture is then extracted with ether in the same way.

Oxidation of Malic and Citric Acid

An aliquot part of the organic acid fraction that contains 0.2 to 2.0 mg. of malic acid (5 cc. are usually sufficient) is diluted to 20 cc. with water, and 3 cc. of 50 per cent sulfuric acid are added. The mixture is boiled gently for 8 to 10 minutes to expel traces of ether, cooled, and 1 cc. of bromine water is added. After 5 minutes the solution is filtered with gentle suction through asbestos in a Gooch crucible into a beaker marked at 35 cc.; interfering impurities are thereby removed. The precipitate is washed with small quantities of water until the filtrate reaches 35 cc., when 2 cc. of 1 *N* potassium bromide are added. The temperature of the solution is then adjusted to 20° to 22° C. and 5 cc. of potassium permanganate previously brought to the same temperature are added. The mixture is allowed to stand in a water bath at 20° to 22° C. for 10 minutes with occasional stirring, and is then chilled to 5° to 10° C. and decolorized with 3 per cent hydrogen peroxide added dropwise with vigorous stirring.

Removal of Pentabromoacetone

The oxidation mixture contains the pentabromoacetone derived from any citric acid present; this is removed by extraction with petroleum ether according to the technic described by Pucher, Vickery, and Leavenworth (*6*). The petroleum ether is washed once with 3 cc. of water and the citric acid equivalent to the pentabromoacetone may be determined as described below.

Determination of Malic Acid

The aqueous solution together with the 3 cc. of wash fluid from the petroleum ether is diluted to 100 cc. and a 25-cc. aliquot is transferred to a 300-cc. Kjeldahl flask. About 25 cc. of water and a few angular quartz pebbles are added. To insure the destruction of hydrogen peroxide about 0.5 cc. of potassium permanganate is then added and the solution is decolorized by the addition of 2 cc. of sodium sulfite solution. The flask is fitted with the distillation tube described by Folin and Wright (*3*). A 250-cc. wide-mouth Erlenmeyer flask charged with 10 cc. of freshly filtered dinitrophenylhydrazine solution and 20 cc. of water is used as a receiver; the end of the distillation tube is dipped beneath the surface of the reagent in the receiver and the flame of a microburner is applied to the flask. Distillation is continued at a rapid rate without cooling the receiver until the volume of solution remaining in the Kjeldahl flask has been reduced to somewhat less than 10 cc. A mark previously placed on the flask with a wax pencil at the 10-cc. point is of assistance. The distillation requires from 12 to 15 minutes. The distillation tube is then rinsed off and the receiver is cooled to room temperature.

The orange precipitate is transferred as completely as possible with water to a small (No. 2) Gooch crucible furnished with an asbestos mat, and is then dried for a short time at 100° to 110° C. Meanwhile the receiver is thoroughly drained, and the last traces of precipitate are taken up in hot pyridine used in several successive portions but not more than 3 to 4 cc. in all. The pyridine washings are transferred to a 25-cc. volumetric flask. The crucible is then fitted into a rubber stopper carried on a cylindrical funnel which is attached to a test tube equipped with a side arm and marked at 20 cc. Boiling pyridine is added in small portions to the crucible, and the contents are gently triturated with a glass rod, after which suction is applied and the pyridine is drawn through each time; three or four washings are usually sufficient to dissolve and transfer all the precipitate to the test tube. The pyridine solution is then added quantitatively to the 25-cc. flask used for the rinsings of the receiver. After being cooled to room temperature the solution is made to volume with pyridine and mixed; it is then allowed to settle or is filtered, if necessary, through soft paper to remove shreds of asbestos.

Either a 2-cc. or a 5-cc. aliquot part of the pyridine solution is transferred to a 100-cc. flask and 50 cc. of water are added, followed by 5 cc. of 5 *N* sodium hydroxide. The solution is then diluted to the mark and the blue color is read in a Pulfrich spectrophotometer using color filter S-57 and a cell length that gives readings between 30 and 80 per cent. In general a 1-cm. or a 3-cm. cell is suitable. The extinction coefficient is calculated and the malic acid equivalent is read from a calibration curve constructed as described in the next section.

The method is satisfactory for the estimation of from 0.1 to 2.5 mg. of malic acid in the 25 cc. of pyridine. If more than 2.5 mg. are found the distillation should be repeated on a smaller aliquot part of the oxidation mixture, but if less than 25 cc. are employed it is necessary to add 1 or 2 cc. of 50 per cent sulfuric acid before distilling, and in any case the aqueous volume in the Kjeldahl flask must be from 40 to 50 cc.

Construction of Calibration Curve

Pure commercial *dl*-malic acid is recrystallized twice from water and dried to constant weight in a vacuum desiccator; exactly 200 mg. of the product are dissolved and diluted to 100 cc. with 1 *N* sulfuric acid. This solvent preserves the malic acid indefinitely.

A 5-cc. aliquot (10 mg.) is oxidized under the conditions described; the oxidation mixture is made to 100 cc. omitting the extraction with petroleum ether, and aliquot parts are distilled into the dinitrophenylhydrazine reagent. Readings of the blue color are obtained using both 2- and 5-cc. aliquots of the pyridine solution, and the extinction coefficients are plotted against the number of milligrams of malic acid in the aliquot of pyridine taken. Several determinations should be made of each point and these should agree within 5 per cent of each other. The average values should give a straight line.

Table I. Calibration Data for Determination of Malic Acid with Pulfrich Spectrophotometer

(Light filter S-57)

Extinction Coefficient	Malic Acid
K	*Mg.*
0.030	0.016
0.039	0.020
0.047	0.024
0.060	0.032
0.078	0.040
0.116	0.060
0.156	0.080
0.200	0.100
0.315	0.160
0.395	0.200
0.473	0.240
0.628	0.320

Table I gives the data of the calibration curve obtained in this laboratory. It represents the average of a large number of closely agreeing determinations obtained in several different ways: (1) From 0.1 to 5.0 mg. of malic acid were separately oxidized and the extinction coefficient was obtained with and without steam distillation of the product of oxidation. When distillation was omitted the dinitrophenylhydrazine was added and the mixture was heated for 10 minutes in a boiling water bath. (2) Ten milligrams of malic acid were oxidized and the resulting solution was diluted to 100 cc.; of this 0.5- to 25-cc. aliquots were analyzed both with and without distillation. (3) Similar experiments were conducted in which from 0.3 to 6.4 mg. of citric acid were added before oxidation, and the pentabromoacetone was subsequently removed by extraction with petroleum ether. In all cases five and usually ten readings of the spectrophotometer were taken and averaged, and readings were usually obtained with

two cells of different lengths. In these observations the extinction coefficient observed for a given quantity of malic acid never varied more than ±8 per cent, and duplicate determinations usually agreed within ±3 per cent. Consistent results were obtained whether the oxidation products were distilled or not, and the presence of citric acid during the oxidation had no effect.

The data in Table I give the extinction coefficient, K, for the number of milligrams of malic acid represented by the 100-cc. volume of blue solution upon which readings are taken. The calculation of the result of an analysis is made as follows:

Grams of malic acid in 2 grams of tissue = mg. of malic acid in

$$Py \times \frac{25}{Py} \times \frac{100}{Ox} \times \frac{100}{Fr} \times \frac{1}{1000}$$

where Py = aliquot of the 25 cc. of pyridine solution
Ox = aliquot of the 100 cc. of oxidation mixture
Fr = aliquot of the 100 cc. of organic acid fraction
To convert into percentage the result is multiplied by 50.

If preferred, calibration curves may be so drawn as to give the malic acid content of the entire 25 cc. of pyridine when a 2-cc. aliquot and a 5-cc. aliquot are taken. The data for these curves may be derived by multiplying the data in column 2 of Table I by 12.5 and 5, respectively.

Discussion

The oxidation of malic acid with potassium permanganate must be conducted with careful attention to the temperature. In a series of experiments carried out at various temperatures with known amounts of malic acid, the yield of product, as measured by the blue color of the alkaline solution of its dinitrophenylhydrazine derivative, was 66 per cent at 9° C., 100 per cent at 19° and at 26° C., 70 per cent at 32° C., and 32 per cent at 40° C. Experience showed that an oxidation temperature within the range 20° to 22° C. gave consistent results and this condition was therefore adopted.

The yield of product is also influenced by the amount of potassium bromide added, being considerably depressed if only 1 cc. of N bromide is added instead of 2 cc. A further moderate excess of bromide, however, did not influence the results. Variations in the amounts of sulfuric acid and of permanganate were without material influence, provided excess of both were present, but the conditions recommended with respect to these reagents have been found advantageous and should be observed.

The removal of the excess of permanganate after the oxidation was found to present some difficulty. Ferrous sulfate was not satisfactory because oxidation mixtures prepared with this reagent gave a large blank when heated with dinitrophenylhydrazine. Sulfites were satisfactory if malic acid alone was to be determined, but if citric acid was present the pentabromoacetone was partly converted into substances that could not be removed with petroleum ether and that subsequently increased the apparent yield of malic acid. Hydrogen peroxide was satisfactory if carefully used. Undue excess must be avoided since, if present under the conditions adopted, a dinitrophenylhydrazine compound soluble in pyridine is produced which increases the amount of blue color observed. The addition of a small amount of permanganate to the solution before distillation provides for the removal of any ordinary excess of peroxide, and the subsequent addition of sulfite removes the excess of permanganate together with any bromine that may have been liberated.

The distillation of the oxidation product with steam effects an important purification of the substance and eliminates the necessity for blank determinations, at least in connection with the determination of malic acid in the leaf tissue the authors have chiefly employed. Before the possibility of this step had been appreciated, it had been necessary to conduct parallel oxidations on equal aliquots of the oxidation mixture, one with and one without potassium bromide. The blank determination usually amounted to the equivalent of from 0.2 to 0.4 per cent of malic acid in the tobacco leaf tissue, but was undoubtedly due to the presence of some other substance. Blanks of a similar order of magnitude were secured when tissue was analyzed from which all the malic acid had been removed by thorough extraction with hot water. This difficulty was completely avoided by the steam distillation of the oxidation product.

Another blank, although of very small magnitude, was eliminated by the aliquoting of the oxidation mixture. The reagents alone give a small but constant blank equivalent to from 0.025 to 0.04 mg. of malic acid in the entire pyridine solution when the whole of the oxidation mixture is distilled; a similar blank is obtained if organic acids are present but potassium bromide is omitted. The amount of color is unreadable, however, if an aliquot of 50 cc. or less of the oxidation mixture is employed, and does not influence the accuracy of the determination of even as little as 0.1 mg. of malic acid. The blank determination in the oxidation mixture does assume importance, however, when tissues very low in malic acid are studied. Such preliminary experiments as the authors have carried out with blood, urine, or muscle extracts have shown that a control oxidation in the absence of bromide is necessary in these cases.

The selection of the proper aliquots to use must be founded on experience. The method is best adapted to the determination of quantities of malic acid not exceeding 2.5 mg. Larger amounts yield a precipitate with dinitrophenylhydrazine that is difficult to manage by the technic described.

The oxidation product of malic acid is stable for many days in sufficiently acid aqueous solution at room temperature, but is unstable in alkali. The pyridine solution of the dinitrophenylhydrazine derivative can be kept for several days if necessary without change. The blue color produced by the addition of alkali is fully developed at once and does not change appreciably for at least 2 hours.

Simultaneous Determination of Citric Acid

The citric acid equivalent of the pentabromoacetone removed by extraction with petroleum ether is best determined by the method recently described by Pucher, Vickery, and Leavenworth (*6*). Certain refinements of this method have been developed to deal with the small quantities of citric acid encountered when the chief object is the estimation of the malic acid.

The petroleum ether extract, obtained as already described, is washed three additional times with 3 cc. of water to remove inorganic halides, the washings being discarded. A 3-cc. quantity of 4 per cent sodium sulfide solution is added to the funnel and, after vigorous shaking, the aqueous layer is drawn off into a 50-cc. Erlenmeyer flask. The petroleum ether is then treated a second time with 3 cc. of sodium sulfide, and is washed three times with 3 to 4 cc. of water, the aqueous solutions being all received in the same flask. To this 2 cc. of 2 N sulfuric acid are added, a few angular quartz pebbles are dropped in, and the solution is boiled gently for 3 minutes to expel hydrogen sulfide. It is then cooled to room temperature, and sufficient 1.5 N permanganate is added to produce a red color (0.8 to 1.0 cc. usually) permanent for 15 to 20 seconds. The color is discharged by the addition of a small excess of halogen-free hydrogen peroxide, and 2 cc. of concentrated nitric acid, 3 cc. of standard silver nitrate, 1 cc. of ferric alum indicator solution, and 3 to 4 cc. of ether are added. The flask is shaken vigorously to coagulate the silver bromide, and the solution is titrated with thiocyanate from a microburet to a faint salmon-pink color. Multiplication of the number of cubic centimeters of silver nitrate used by the factor 1.12 gives the number of milligrams of citric acid in the aliquot of the organic acid fraction taken. If the solution should chance

to contain in excess of 3 mg. of citric acid the first drop of thiocyanate will produce a red color. In these circumstances additional silver nitrate is added and the titration is completed in the usual way.

Recovery of Malic Acid

Table II gives the data of analyses of a solution of pure malic acid. The values of the extinction coefficient as observed in cells of two lengths are shown, and the malic acid equivalent to the average of these is given as closely as it could be read from the calibration curve.

Table II. Recovery of Malic Acid

(Light filter S-57)

Malic Acid Taken	K 1-cm. cell	K 3-cm. cell	Malic Acid Found	Recovery
Mg.			*Mg.*	%
0.20	0.032	0.031	0.20	100
	0.029	0.031	0.20	100
0.50	0.079	0.077	0.50	100
	0.082	0.081	0.51	102
	0.074	0.075	0.48	96
1.00	0.153	0.152	0.97	97
	0.168	0.158	1.03	103
	0.158	0.155	1.00	100

In Table III are data on further analyses; the first five determinations were made on solutions that were subjected to the complete procedure—that is, the malic acid was extracted with ether in the customary way and every successive step was carried out. The next group of determinations was on aliquots of a standard solution to which 25 mg. of a mixture of oxalic, lactic, pyruvic, succinic, tartaric, maleic, glycollic, and fumaric acids in approximately equal amounts had been added. The last determinations were conducted in the presence of 6.4 mg. of citric acid.

Table III. Recovery of Malic Acid

Malic Acid Taken	Mixture of Other Acids Taken	Citric Acid Taken	Malic Acid Found	Recovery
Mg.	*Mg.*	*Mg.*	*Mg.*	%
2.00	..	...	2.10	105
4.00	..	...	4.00	100
100.0	..	...	104.0	104
100.0	..	...	101.0	101
100.0	..	...	106.0	106
0.0	25	...	0.00	...
0.0	25	...	0.03	...
1.0	25	...	1.00	100
1.0	25	...	1.08	108
0.1	25	...	0.09	90
0.1	25	...	0.11	110
2.0	..	6.4	1.96	98
2.0	..	6.4	2.04	102

Table IV illustrates the recovery of malic acid added to tobacco leaf tissue. The malic acid content of each sample of the tissue was first ascertained by the present method; additions of malic acid were then made, and the complete analysis was conducted. The results are expressed in milligrams per 2 grams of tissue and show excellent recoveries and close reproducibility.

Table IV. Recovery of Malic Acid Added to Dry Tobacco Leaf Tissue

(Figures are milligrams per 2-gram sample)

Added	Originally Present	Found	Recovered	Recovery
Mg.	*Mg.*	*Mg.*	*Mg.*	%
80.0	20.8	103.5	82.7	103
80.0	15.0	91.2	76.2	95
100.0	26.4	135.0	108.6	109
100.0	26.4	124.0	97.6	98
100.0	26.4	126.0	99.6	100
100.0	26.4	130.0	103.6	104
100.0	26.4	123.0	96.6	97
2.0	26.4	28.3	1.9	95
4.0	26.4	30.4	4.0	100

As a further test of the reliability of the present method, a number of samples of tobacco leaf tissue were analyzed for malic acid by the polarimetric method of Dunbar and Bacon (*2*), as modified by Vickery and Pucher (*9*). The results in Table V show a satisfactory agreement between the two methods. The oxidation method in all but one case gave slightly higher results. The data illustrate the wide differences in malic acid content that may be encountered in this tissue, and provide evidence that little, if any, optically inactive malic acid occurs in the tobacco plant.

Table V. Comparison of Oxidation and Polarimetric Methods for Malic Acid

Sample	Oxidation Method	Polarimetric Method
	%	%
Fresh leaf I after extraction with water	0.00	0.00
Fresh leaf F.L. after extraction with water	0.10	0.00
Cured leaf 584	1.02	0.95
Cured leaf 594	4.76	4.00
Cured leaf 582	0.88	0.86
Partially cured leaf I	3.04	2.88
Partially cured leaf H	4.08	3.93
Partially cured leaf A	8.14	8.34
Partially cured leaf E	6.48	6.20
Fresh leaf F.L.	9.64	9.53

The oxidation method to determine malic acid has been chiefly employed in this laboratory in the study of tobacco leaf and stem tissue. Preliminary experiments with other plant tissues have given equally satisfactory results, however, and there seems no reason to suppose that the method cannot be generally applied. Successful analyses have also been conducted on blood, urine, and muscle extracts, and experiments with aspartic acid have shown that this amino acid can be accurately determined, if deaminized with nitrous acid previous to the oxidation.

Acknowledgment

The expenses of this investigation were shared by the Connecticut Agricultural Experiment Station and the Carnegie Institution of Washington.

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Preparation of Sintered Pyrex Glass Filters

Sir: Attention of research workers was called in your Analytical Edition of March 15, 1934, to the preparation of fritted glass filters by an article on page 154 of that issue by Kirk and his coworkers at the University of California. Unfortunately, Kirk neglected to mention that the filters he described are covered by patents throughout the world and, in the United States, by Patent 1,620,815 issued to Herschkowitsch and Prausnitz and by them assigned to this company. Obviously your readers should be appraised of this fact for their protection and our own.

Jena Glass Works, Schott & Gen.

Jena, Germany
May 28, 1934

Volumetric Estimation of 5-Bromo-2-Furoic Acid with Standard Bromate

Elizabeth E. Hughes and S. F. Acree, Bureau of Standards, Washington, D. C.

In a preceding article (*4*) the authors described the equipment, technic, and conditions for allowing furfural to react quantitatively with one molecule of bromine from standard bromate within 5 minutes at 0° C. with errors less than 0.5 per cent. The method is especially useful in the analysis of farm wastes for pentosan content. The usual procedure (*1*) is to distill the fibers with 12 per cent hydrochloric acid and determine the volatilized furfural with phloroglucinol, thiobarbituric acid, or with excess bromine by the method of Powell and Whittaker (*5*). The errors, even with empirical corrections, may be 2 to 4 per cent. The technic of the bromination method cited above is more nearly accurate and takes much less time.

In an attempt to apply this method to the analysis of products of bromination and oxidation of furfural, the present investigation was undertaken to see whether 5-bromo-2-furoic acid can be determined quantitatively both by titration with standard alkali and by addition of molecular equivalents of bromine.

Experimental Procedure

The 5-bromo-2-furoic acid was first described by Hill and Sanger (*3*) with melting point of 184° to 186° C. It is isomeric with a monobromo derivative having the bromine in the 3 or β position with melting point of 128° to 129° C. The acid used in these experiments was kindly made for the authors by J. A. V. Turck by the method of Gilman and Wright (*2*), and was a white crystalline substance melting at 184° to 186° C. The purity based upon acidity by titrating with 0.1 *N* or 0.02 *N* sodium hydroxide using phenolphthalein as indicator was 100 per cent (±0.1 per cent). The solubility in water was determined as approximately 2.5 mg. per ml. at ordinary room temperatures.

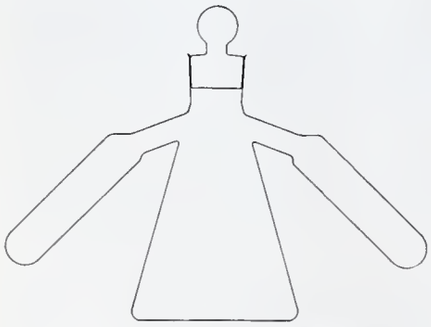

Figure 1. Diagram of Flask

For these experiments the solution of the acid was prepared by dissolving 2 grams of the acid in 1 liter of boiling water which was kept warm until solution was complete, then cooling to room temperature. An aliquot portion of the solution was transferred to the body of a special side-arm titration flask (Figure 1) containing 200 ml. of 3 per cent hydrochloric acid (prepared by diluting 1 part of 36 to 38 per cent concentrated hydrochloric acid with 11 parts of water). In one side arm were placed 25 ml. of 0.1 *N* aqueous solution of potassium bromate containing 50 grams per liter of potassium bromide. In the other side arm were placed 10 ml. of an aqueous solution of 10 per cent potassium iodide. A second flask was similarly prepared but omitting the 5-bromo-2-furoic acid. The flasks were sealed by placing a drop of phosphoric acid on the ground-glass stopper; the flask and contents were allowed to come to constant temperature. The experiments at 0° C. were made with the flasks suspended in an ice bath for the short time periods and placed in an ice box maintained at 0° C. for the longer ones. Experiments at 21° C. were conducted in a constant-temperature room. The temperatures mentioned above are subject to fluctuations of not more than 2° C.

The potassium bromate solution was introduced from the side arm into the acidified 5-bromo-2-furoic acid by tilting and the solutions were mixed by swirling the flask gently. The reaction was allowed to proceed for definite time periods, at the end of which the potassium iodide was added. At ordinary laboratory temperature about 10 minutes seems to be ample duration for the reaction. The contents were shaken vigorously and the liberated iodine titrated with 0.1 *N* sodium thiosulfate using starch indicator (0.5 grams of soluble starch in 250 ml. of boiling water).

Table I. Reaction of 5-Bromo-2-Furoic Acid with Bromine

Time of Reaction	Weight of Sample: 103 mg.	85 mg.	50 mg.	62 mg.	46 mg.	26 mg.
	Per cent of theoretical amount found					
	21° C.			0° C.		
Sec.						
30	61.7	63.2	...	...	...	...
Min.						
1	81.6	83.8	...	...	...	...
2	92.3	95.7	99.0	...	...	...
3	...	...	...	63.1 65.9	...	52.4
4	97.7	98.9	100.0	...	...	...
5	...	...	...	...	...	86.3
6	99.0	99.8	100.1	...	...	...
8	99.8	100.0	100.1	...	...	...
10	100.0	100.2	100.1	...	92.8	93.6
20	100.1	100.6	100.5	98.3	(85.3)	97.8 99.3
30	100.0	100.5	100.6	...	...	...
40	...	...	...	...	99.6	99.8 99.7
60	100.0	100.6	102.3	...	(93.7)	98.5 100.6
90	...	...	...	100.6 (75.8)	...	99.9 100.7
Hrs.						
2	101.1	...	...	...	100.1 (97.8)	...
5	...	...	...	...	...	103.4
18	...	...	...	103.3	101.9 100.5	102.9
20	101.2	102.1	...	...	...	...
Days						
3	103.0	...	...	...	...	...
7	105.2	...	...	...	...	...

The results at 0° and 21° C. are shown in Table I and Figure 2 and express the extent of the reaction with respect to time. The addition of 2 moles of bromine to 1 of 5-bromo-2-furoic acid is represented by 100 per cent. The number of

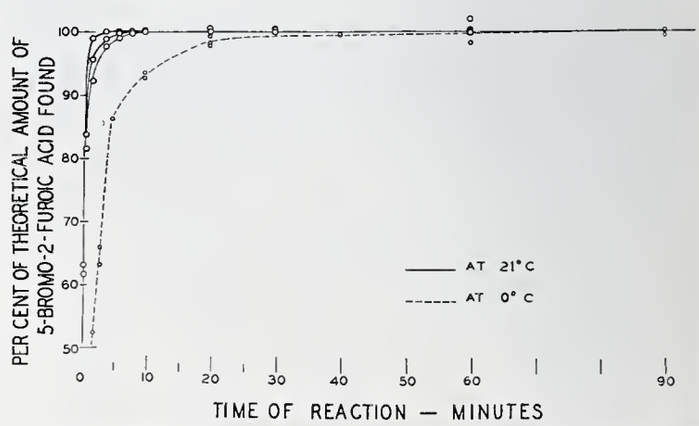

Figure 2. Reaction of 5-Bromo-3-Furoic Acid with Bromine

milliliters of 0.1 *N* thiosulfate required for the blank less that required for the sample multiplied by 0.004775 gives the number of grams of 5-bromo-2-furoic acid.

Discussion of Results

Table I and Figure 2 show the rate of addition of bromine under specified conditions upon which basis the percentage of the theoretical amount found is calculated. It is found that bromine adds so rapidly to 5-bromo-2-furoic acid that, in contrast to furfural (*4*), it is not practical to stop the reaction short of two molecular equivalents of the halogen. Over a period of several hours and days the tetrabromide addition product of the normal reaction apparently loses hydrobromic acid very slowly to form more double bonds and the bromine used in subsequent reaction may reach 0.1 mole or more. According to the mass law and verified in Table I and Figure 2, the percentage of normal and of further reaction with the same amount of bromine for a given short time period should increase with decrease in size of sample.

At 0° C. the results are not always reproducible, as shown by the percentages given in parentheses. Experiments to be reported later show a small photochemical effect which is not, however, responsible for the discrepancies in the analyses, especially at 0° C. At 21° C., however, the results are concordant and the reaction, regardless of the size of the sample, is complete within 8 to 30 minutes.

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Continuous Determination and Recording of Carbon Dioxide Content of Gas Mixtures

Apparatus Used in the Bureau of Mines Helium Plant

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In designing an apparatus to give a continuous record of the carbon dioxide content of helium-bearing natural gas processed in the Amarillo Helium Plant of the Bureau of Mines, three methods were investigated. One, described by White, based on conductance measurements, was selected as being most suitable for the application desired. A modification of this method, which improves its operation and adaptability in plant installation, is briefly described. The apparatus, as modified, has given satisfactory service in a plant installation for recording concentrations of carbon dioxide from 0.1 to 1.0 per cent in sweet natural gas.

The determination of carbon dioxide in gas mixtures by absorption in alkaline media has occupied the attention of a large number of investigators since Dalton originated the method. The literature has been adequately reviewed, most recently by Thomas (*9*) and by Martin and Green (*3*). The latter authors also classify and discuss briefly the methods which have been used. An improvement in pH measurement has been published by Wilson, Orcutt, and Peterson (*11*), who describe a potentiometric method for determination of carbon dioxide.

At the Amarillo Helium Plant of the Bureau of Mines the need arose for an accurate apparatus to record continuously and automatically the carbon dioxide content of helium-bearing natural gas. The average carbon dioxide content of the unprocessed gas is about 0.7 per cent, and the hydrogen sulfide content less than 0.002 per cent. The other constituents vary somewhat, depending upon the proportion of the total flow produced from each of the government's gas wells and upon temperature conditions in the pipe line. Because of this low concentration of carbon dioxide and variation in other constituents the gasometric methods and those based on physical properties of the gas could be eliminated at once in considering the known continuous, recordable processes. Three types of electrolytic methods offered possibilities and were investigated.

Measurement of Carbonate-Bicarbonate Equilibria

First Method. Two variations of a method depending upon measurement of the equilibrium between carbonate and bicarbonate salts of the alkalies or alkaline earths, as affected by the partial pressure of carbon dioxide in equilibrium with the solution, have been developed. The earlier process determined the equilibrium by colorimetric measurement of the pH of the solution. The relatively low accuracy inherent in this method has been improved upon by the use of the glass electrode to determine the pH potentiometrically (*11*), adding rapidity and simplicity to a method which has advantages in being independent of gas flow.

Continuous measurements of the pH of a solution are practicable only with the quinhydrone and antimony electrodes.[1] The latter has the advantage of not requiring the addition of any reagents for the measurement but offers some difficulties in preparation and calibration for use with alkaline solutions which are in motion and are not in contact with air. The quinhydrone electrode has a limited range because of decomposition and oxidation which occur in the system when subjected to alkaline solutions. It has been applied without success in an attempt to measure carbonate-bicarbonate equilibria (*11*). This type of electrode is not suitable for use in unbuffered solutions, but since a decided change in pH will be caused by a trace of carbon dioxide in a perfectly neutral salt it seemed desirable to make some very brief tests of the pH in unbuffered solutions. The results of this limited study were not satisfactory, showing excessive drifting of the

[1] After completion of the experimental work on which this paper is based, an article by Vickers, Sugden, and Bell appeared in *Chemistry & Industry*, **51**, 545 (1932), reporting an apparatus for the continuous recording of pH in which a glass electrode is used.

potential, as would be expected, and slow attainment of equilibrium.

Second Method. A continuous record of the carbon dioxide content of a gaseous mixture has been obtained by Gordon and Lehmann (*2*), who used a recording alternating current milliammeter to measure the electrolytic conductance of a barium carbonate–bicarbonate solution in equilibrium with carbon dioxide. To determine the operating characteristics of this method and its adaptability to the immediate requirements an apparatus was constructed similar to that used in the work of the authors mentioned above. The recommended gas flow and temperature of operation were employed, but a smaller volume (15 cc.) of saturated barium carbonate was used, since it was believed that equilibrium in the apparatus would be attained more quickly. The measuring circuit consisted of an alternating current indicating milliammeter in series with the conductance cell and with a 110-volt, 60-cycle source of current.

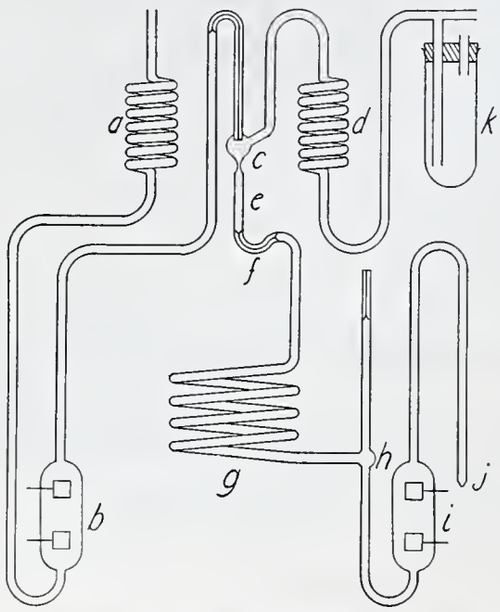

Figure 1. Schematic Diagram of Apparatus

Gordon and Lehmann (*2*) found the time lag of their apparatus to be of the order of one minute at 50° C. In the apparatus constructed for preliminary tests in this laboratory the time to reach equilibrium, which is an indication of the usefulness of the apparatus, was 10 to 20 minutes, depending upon the carbon dioxide concentration. Although the device is simple, the method was not considered suitable because of the time lag.

Measurement of Neutralization of a Hydroxide by Electrical Conductivity

Third Method. The third type of electrolytic method investigated was a direct measurement of the change in conductance of a solution of an alkaline or alkaline earth hydroxide accompanying the formation of a carbonate. A brief theoretical discussion of the method has been given by Smith (*6*).

Martin and Green (*3*) state that the method was devised by Cain and Maxwell (*1*), although Taylor and Taylor (*8*) give priority to Rideal and Taylor (*4*) by stating that in 1918 they "published the first account of gas analysis on the electrolytic principle." It has been useful in determining small percentages of carbon dioxide by cumulative absorption at constant gas flow, measuring the rate of change of conductivity. A recording instrument has been employed by Thomas (*9*) in measuring the conductivity of a sodium hydroxide solution used for the continuous absorption of carbon dioxide from a measured volume of air, and by Spoehr and McGee (*7*) with barium hydroxide. Both developments were designed to measure atmospheric carbon dioxide.

White (*10*) has developed an ingenious apparatus suitable for the analysis of various percentages of carbon dioxide as well as a number of other gases. His device is a simplification of the carbon monoxide recorder described by Taylor and Taylor (*8*) who developed, and applied for a patent on, a fluid proportioning device. The novelty of their apparatus consisted in this method of securing accurate mixtures of gas and reagent. A disadvantage of both devices is the use of direct current for the conductance measurements, making recording of the measurements not readily applicable, and introducing the possibility of error from polarization of the electrodes. A modification of White's apparatus was constructed and found to operate satisfactorily with natural gas containing 0.7 per cent carbon dioxide and with atmospheric carbon dioxide. It was not so satisfactory with the gas which had passed through the carbon dioxide–removal system of the Amarillo Helium Plant, possibly because of minute traces of other soluble constituents in the gas, which contained only a trace of carbon dioxide. The modified apparatus differs from that of White's in three particulars:

1. Two conductivity cells are used, relative measurements being made with a Wheatstone-bridge circuit.
2. Alternating current is used for the conductivity measurements.
3. The apparatus operates under a small pressure differential.

A schematic diagram of the apparatus is shown in Figure 1.

Description of Apparatus

The absorbing solution of 0.025 *N* potassium hydroxide is siphoned at a constant-pressure head from a 20-liter reservoir (not shown) through temperature-equalizing coil *a* into reference cell *b*. The solution then drops at a predetermined rate into bulb *c*, trapping a sample of gas, which enters through coil *d* in tube *e*. Goose-neck *f* is adjusted so that each drop will halt, making it necessary for a succeeding drop to form and push the sample of gas and the preceding drop down into absorption coil *g*. The gas and liquid separate at *h*, the solution, after absorption of the carbon dioxide, passing into measuring cell *i* and being discharged from the siphon at *j*. Trap *k* maintains constant pressure on the apparatus with an excess gas flow. As constructed in this laboratory, the entire apparatus is operated in a large Dewar vessel used as a water thermostat.

For convenient plant installation 110-volt, 60-cycle current is used, from which are obtained 6 volts for the Wheatstone-bridge conductance-measuring circuit. The use of two cells allows relative measurements to be made of the change in conductance due to the absorption of carbon dioxide, and partially compensates for variations in temperature, voltage, and concentration. A Leeds & Northrup potentiometer recorder was adapted (*6*) for use in recording the carbon dioxide concentration. Two ranges are available: one from 0 to 1.0 per cent and a low range from 0 to 0.2 per cent of carbon dioxide. The range of the recorder is conveniently changed by means of a double-pole, double-throw switch which changes the galvanometer and slidewire shunts of the recorder. A wiring diagram is given in Figure 2.

Calibration of Apparatus

Two methods are available for calibration. White recommends an empirical calibration for mixtures containing 5 per cent or more of the gas sought, or in cases where absorption is incomplete. When the sample contains less than 2 per cent of the soluble constituent a calibration from conductance data is said to be capable of great accuracy. The latter method of calibration was undertaken for the purpose

of determining the capacity and probable range of the apparatus, the effect of variations in operating conditions, and as a guide in the design of the electrical circuit before construction was completed. This calibration followed White's procedure for obtaining the volume of the drop and the volume of gas aspirated per drop, a and b, respectively, in his notation. After obtaining the number of moles of dry gas m pumped per stroke, the method is somewhat different.

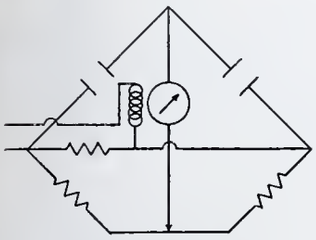

FIGURE 2. WIRING DIAGRAM

Experimental values for a, b, and m were 0.0993 cc., 0.958 cc., and 3.34×10^{-5} moles, respectively, at 25° and 670 mm. An equation, specific for the apparatus, correlating conductivity and carbon dioxide concentration under any conditions facilitates calibration. This is derived as follows:

$$m = \frac{0.958 \times 273\ (P - p)}{22420 \times 760 \times T}$$

$$N_{K_2CO_3} = n = \frac{0.958 \times 273\ (P - p) \times 138.21 \times 1000 \times P_{CO}}{22420 \times 760 \times T \times 0.0993 \times 69.105 \times P}$$

$$n = \frac{0.3091\ (P - p)P_{CO_2}}{TP}$$

where P = pressure in mm.
p = vapor pressure in mm.
P_{CO_2} = partial pressure of carbon dioxide in mm.
T = absolute temperature
$n = N_{K_2CO_3} = N - N_{KOH}$ in gram equivalents per liter
$N = N_{KOH}$ at 0 per cent carbon dioxide

The specific conductance k of any mixture is

$$k = 0.253\ (N - n) + 0.1205\ n$$

$$= 0.253 \left[N - \frac{0.3091\ (P - p)P_{CO_2}}{TP} \right] + 0.1205 \left[\frac{0.3091\ (P - p)P_{CO_2}}{TP} \right]$$

$$= 0.253N - \frac{0.041\ (P - p)P_{CO_2}}{TP}$$

To determine the effect of the variables in the equation, it was differentiated with respect to P, T, and N and the differential equations integrated to obtain the pressure, temperature, and concentration coefficients. The first two coefficients are negligible, but the latter is considerable, indicating that care must be exercised in preparing a carbon dioxide–free potassium hydroxide solution, unless the two cells are identical so that compensation will be perfect.

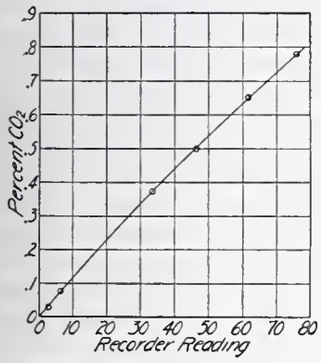

FIGURE 3. CALIBRATION DATA

The calibration from conductance data was obtained only as a guide during construction, and in the arrangement of the electrical circuit of the recorder. For use in plant operation an empirical calibration was made by using standard samples of natural gas containing various percentages of carbon dioxide. The concentration of carbon dioxide was determined by absorption in barium hydroxide with subsequent titration, using thymolphthalein as the indicator, as recommended by Schollenberger (*5*). The calibration data, using standard samples, are plotted in Figure 3. A comparison of curves plotted from empirical and calculated data showed a constant percentage deviation, indicating systematic errors in the calibration from conductance data. Although the relation between conductance and concentration of carbon dioxide is a straight line, resistance, the reciprocal of conductance, is a hyperbolic relation; hence, the curves are hyperbolic.

OPERATION OF APPARATUS

As mentioned by White (*10*), the apparatus is somewhat fragile, but, securely mounted and enclosed in a cabinet, it has proved satisfactory for industrial process control. The attention required is limited to renewal of the potassium hydroxide solution at weekly intervals and occasional checking of the gas-aspirating device and the zero point. Excessive vibration will interfere with a steady rate of gas sampling and must be avoided.

The lag of the apparatus was determined to be approximately 3 minutes, which may be reduced, if desirable, by increasing the rate of flow of the reagent. There should be no possibility of incomplete absorption with the low carbon dioxide–content gas at any rate of flow possible with the apparatus. The spiral absorber has been shown (*3*) to be a highly efficient scrubbing device, and, moreover, the absorbent is but 25 per cent exhausted at the maximum of the range of carbon dioxide. To check the completeness of absorption, however, a qualitative test was made, by passing the gas from the apparatus through a barium hydroxide solution, which showed complete absorption in the apparatus.

The apparatus whose calibration was described by White was stated to have a sensitivity of about one volume of carbon monoxide (or carbon dioxide) in ten thousand of the mixture in the range 0 to 2 per cent. This degree of precision was not required in the apparatus which has been described. In the range 0 to 1 per cent carbon dioxide, the recorder is easily sensitive to one division, or about 0.01 per cent. The analyses of the gas samples which determined the calibration were readily reproducible to 0.01 per cent. Some unaccountable factors may also affect the precision of measurement, but an assumed accuracy of one part in five thousand is considered to be well within the limits of error.

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SOLID CARBON DIOXIDE IN GERMANY. Germany, like European countries generally, lags far behind the United States in the use of this product. High cost, climatic conditions, absence of extremely hot weather, and smaller consumption of ice cream and iced foodstuffs generally, coupled with transportation difficulties, have retarded development. Manufacture, nevertheless, is making steady gains. The Mannesmannroehren-Werke is constructing a plant at its limestone works in Neandertal, utilizing the carbon dioxide gas produced in burning lime.

Occurrence of Selenium in Pyrites

Kenneth T. Williams and Horace G. Byers, Bureau of Chemistry and Soils, Washington, D. C.

THE work of Kurt W. Franke, state chemist of South Dakota, which traced the causes of a certain animal disturbance, locally known as alkali disease, to the vegetation grown upon certain definite soil areas, and the subsequent detection in the Bureau of Chemistry and Soils of selenium in the vegetation of these areas has led to a series of investigations upon selenium. In the course of these investigations the presence of selenium has been traced from plant to soil and from soil to its parent shales.

Among the shales known to contain selenium is the Pierre shale, in certain sections of which occur nodules of iron pyrites. One of these nodules, collected by one of the writers, was found to contain 205 parts per million of selenium. This is a greater concentration of selenium than has been found in any other portion of the shale, some hundreds of samples of which have been examined in this laboratory. This fact, coupled with the known occurrence of selenium in chamber sulfuric acid made by roasting pyrites, and the historical fact that selenium was discovered, in 1817, in the sulfuric acid chambers in which the sulfur dioxide used was derived from certain copper pyrites (*2*), made it of interest to determine how general the association of sulfur and selenium in pyrites may be. There was also the added incentive that over the area of soils known to be derived from the Pierre shale, the presence of selenium in both soil and vegetation had been determined to be of general occurrence.[1] These soils all occur in arid or semi-arid areas. If selenium occurs in pyrites in general, the fate of the selenium in humid areas, as contrasted with its disposition in arid areas is of striking interest in relation to the whole selenium problem. Initial data were secured through the analyses by W. O. Robinson of the samples indicated in Table I.

Table I. Selenium in Selected Samples of Pyrites

Sample	Source	Selenium Content
		P. p. m.
Concretionary pyrite	Fischer's Gully, Nebr.	205
Massive pyrites	Brigham, Utah	15
Crystals of pyrite	Saratoga, Colo.	10
Crystals of pyrite	Isle of Elba	Trace
Mispickel	Paris, Me.	Trace

With these facts in mind, T. D. Rice, of the Soil Survey, was requested to locate a number of sources of pyritiferous materials in the humid area of the eastern portion of the United States. In 1917 a survey of available pyrite sources was published by Smith (*4*), and through this a number of the sources of pyrite listed below were located and samples collected by Rice and Byers.

Other samples were secured from a pyritiferous clay deposit near Bay Springs, Miss. A sample of concretionary pyrite was secured by S. A. Swenson from the Selma chalk of Alabama, and samples of pyrite and of limonite pseudomorphs after pyrite through the courtesy of W. H. Sage of the Alberene Company of Schuyler, Va. In addition to the pyrite samples a number of samples of soil and of other materials presumably derived from materials of pyrite content were also secured.

These samples were all examined quantitatively for their selenium content by the appropriate one of the methods outlined by Robinson, Dudley, and Williams (*3*). The results obtained are given in Table II. Where only whole number values are given, the accuracy does not exceed 2 parts per million.

[1] Unpublished data, Bureau of Chemistry and Soils.

No attempt has been made to determine the sulfur content of the pyritiferous material of the samples reported in Table II. The ores were far from pure pyrites and in no case is there any guarantee that they may be represented by any definite formula. It is probable, however, that the mean sulfur content is not more than 40 per cent, corresponding to 400,000 parts per million. The mean selenium content is 59.0 parts per million. The ratio of sulfur to selenium is, therefore, of the order of 6×10^3. The mean ratio of sulfur to selenium in the earth's crust is, according to Clark and Washington (*1*), about 10^6. Both these quantities are of course a rough approximation, but even so, it is evident that in this series of minerals there is a very marked concentration of selenium.

Table II. Selenium Content of Pyrite and Associated Materials

Lab. No.	Type of Material	Location	Selenium Content
			P. p. m.
B-3179	Marcasite in black clay	Bay Springs, Miss.	0.3
B-3183	Marcasite in clay	Bay Springs, Miss.	0.6
B-3174	Concretionary pyrite in Selma chalk	Livingstone, Ala.	8
B-3192	Pyrite	Pyriton, Ala.	75
B-3196	Pyrite	Bremen, Ga.	8
B-3197	Pyrite	Draketown, Ga.	50
B-3199	Pyrite	Villa Rica, Ga.	45
B-3202	Pyrite	Dallas, Ga.	250
B-3203	Pyrite	Marietta, Ga.	110
B-3204	Pyrite	Marietta, Ga.	150
B-3205	Pyrite	Marietta, Ga.	180
B-3207	Pyrite	Ball Ground, Ga.	80
B-3169	Pyrite	Crouse, N. C.	10
B-3170	Pyrite (partially decomposed)	Crouse, N. C.	55
B-3171	Pyrites	Crouse, N. C.	50
B-3209	Pyrrhotite	Ducktown, Tenn.	5
B-3210	Chalcopyrite	Ducktown, Tenn.	10
B-3211	Pyrite	Ducktown, Tenn.	1
B-3212	Pyrite	Mineral, Va.	15
B-3213	Pyrite	Mineral, Va.	65
B-3215	Pyrite	Madison, Va.	0
B-3216	Pyrite	Dumfries, Va.	125
B-3464	Pyrite in serpentine	Schuyler, Va.	75
B-3465	Pseudomorphs after pyrites	Schuyler, Va.	45
		Av.	59

It would appear, therefore, that in the hydrolysis of pyritiferous material to produce soil, the selenium content, when conditions are not favorable for removal of both sulfur and selenium, should be higher than in soils derived from other sources. It is to be expected that the processes which convert pyrites to limonitic material accompanied by oxidation of the sulfur to sulfuric acid will cause a like transformation of selenium to soluble form. If these processes are accompanied by leaching both selenium and sulfur should be almost completely removed from the soil produced. This should be the case in humid areas. On the contrary, in arid or semi-arid areas where little percolation accompanies soil formation, pyritiferous soil parent material should result in a soil which, along with a high sulfur content, should have appreciable selenium content. This appears to be the case in the soils derived from the Pierre shale. In this shale the selenium content varies between wide limits, a range from traces up to 103 parts per million having been observed. In soils derived from these shales, in an area of present mean annual rainfall of 15 inches, selenium has been found as high as 32 parts per million.

In soils of humid areas selenium has been found only in traces, though it must be confessed that no extensive examinations have as yet been made. A little light is thrown upon the fate of selenium in soil formation under humid conditions by the data given in Table III.

Table III. Selenium Content of Sections of a Clay Bed near Bay Springs, Miss.

Lab. No.	Material	Selenium Content
		P. p. m.
B-3175	Surface soil	0.0
B-3176	Yellow sand (0–6 ft.)	0.0
B-3176a	Limonite scales in sand	0.4
B-3177	Yellow sand (6–20 ft.)	0.1
B-3178	Iron stone cap of clay	0.3
B-3187	Yellow clay beneath cap	0.4
B-3179	Black clay with pyrites	0.3
B-3183	Pyrites scale	0.6
B-3180	Light-colored scale	0.15
B-3182	Weathered black clay	0.15
B-3181	Weathered mixed clay	0.20
B-3185	Concentrated extract of weathered clay	0.01

The samples reported in Table III were obtained from a deposit which is being used as the source of supply of a "medicine." The clay bank has been excavated to a depth of about 50 feet. The over-burden is a yellow sandy clay of a maximum depth of about 25 feet. On parts of this sandy slope small pillars of clay are capped with thin scales of limonitic material. Below the sandy layer is a crust of limonitic material about 2 inches thick. This crust is apparently a partly hydrolyzed pyrite layer. Immediately below this crust is a thin layer of yellow clay. Below the yellow clay is a 3-foot layer of dense black clay containing large numbers of small crystals of marcasite. Below the black clay is a very thin layer of scale consisting largely of marcasite. Below this, and of a thickness not determined, is a deposit of clay somewhat lighter in color than the black clay and containing much smaller quantities of pyrites. The clay layers are used for the preparation of the above mentioned medicine by being allowed to dry and weather, under cover, for a year or more. The weathered material, which contains considerable quantities of ferrous sulfate, is leached with water.

It is unfortunate that this deposit is so low in selenium content, since otherwise it offers a very favorable set of conditions for tracing the course of the selenium in weathering. It is, however, clear that the soil proper is essentially free from selenium, that the weathering produces water-soluble selenium removable by leaching, and that the removal of selenium from the limonitic material does not keep full pace with the removal of the sulfur. This last fact is also indicated by B-3465 of Table II. In this sample nearly all the sulfur is removed while a considerable selenium content remains.

The transfer of selenium by leaching of weathered products, and its relation to sulfur translocation, are also indicated by the presence of selenium in certain shallow wells in the Pierre shale. These waters are high in sulfate content and selenium has been found in quantities as high as 0.07 part per million. The presence of selenium in gypsum deposits in weathered Pierre shale has also been determined in quantities ranging from 5 to 15 parts per million.[2]

A small number of shales were also collected and their selenium content determined in Table IV.

Table IV. Selenium Content of Alabama Shales

Lab. No.	Material	Location	Selenium Content
			P. p. m.
B-3191	Dark calcareous shale	3 miles south of Desmopolis	0.6
B-3188	Dark shale	Leeds	0.15
B-3189	Ferruginous shale	Leeds	0.20
B-3190	Dark shale	Leeds	0.15
B-3195	Light shale	Heflin	0.15

General Remarks

It would appear from the data above presented, supplemented by a mass of unpublished data on file in this bureau, that selenium is of much greater distribution in soils and vegetation than has heretofore been suspected. It seems probable that in arid and semi-arid areas the presence of selenium is to be expected in every case where the sulfur content of the soil parent material is high and that, where the selenium content permits, the derived soils and their vegetation may contain sufficient selenium to render them potentially dangerous. The mere presence of selenium in soil is not to be considered an indication of an inferior soil. It also seems probable that soils produced in humid areas are not likely to have a pernicious selenium content even though the parent materials are relatively rich in this element.

If the above inferences be warranted, it would appear that investigations of the selenium contamination of soils should be greatly broadened in scope, and that, in particular, they should cover soils which are to be used under irrigation.

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Received March 24, 1934.

[2] Unpublished data, Bureau of Chemistry and Soils.

Constant-Feed Buret and Apparatus for Catalytic Dehydration of Alcohols

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In many reactions a constant rate of liquid feed is desirable and it is impossible to obtain an even flow of liquid by means of an ordinary glass stopcock. The apparatus described below will deliver liquid at a constant rate over any desired length of time. It operates on the principle of opposing a constant liquid head to a constant resistance. Somewhat similar devices have been described by Sabatier (*1*) and by Vaughen (*2*).

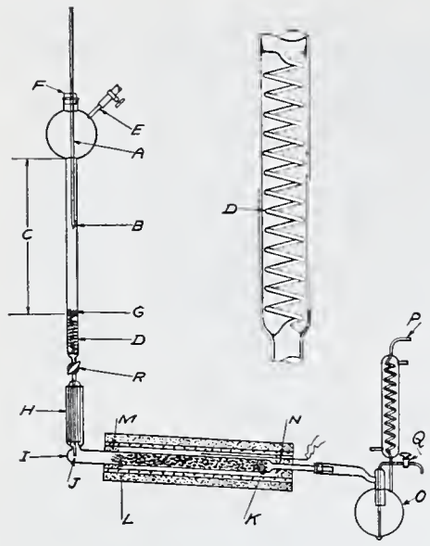
The liquid reservoir of the constant feed-buret is essentially a Mariotte bottle, and the head of liquid can be varied at will by raising or lowering tube *A;* the effective head is at *B*, the lower end of tube *A*, and the range through which the head can be varied depends on distance *C*. The constant resistance is furnished by capillary spiral *D* through which the liquid must travel. The choice of feed rate is wide, depending as it does on two variables, the liquid head and the resistance, the latter being governed by the length and the bore of the capillary.

For an all-round buret capable of delivering from 15 to 60 cc. per hour, the capacity of *A* is 500 cc., the length of *C* is 60 cm., the bore of capillary *D* is 0.25 to 0.5 mm., and the length of the capillary is 40 cm., the vertical height of the spiral being 5 cm. Tube *E* is of convenience in venting the pressure caused by the insertion of stopper *F*, and with liquids which tend to deposit solid matter, it is well to protect the capillary by a small filter plug of cotton, *G*.

Catalytic Dehydration of Alcohols

This apparatus has a general application for catalytic reactions in which a liquid is vaporized and the resulting gas passed over a solid catalyst. It is especially convenient for the dehydration of alcohols over alumina.

The buret is connected to the catalyst tube by means of mercury seal *H*, which is designed along the conventional lines of a mercury seal for a mechanical stirrer. The alumina catalyst is introduced through the open end of the tube at *I*, which is then



sealed. The charging rate is visible at *J*. The catalyst is held in place by a perforated glass partition at *K* and by a plug of glass wool at *L*. Heat loss is cut down by the insertion of asbestos packing at *M* and *N* into the annular space between the catalyst tube and the furnace block. Receiver *O* can be emptied without dismantling the apparatus, by application of pressure at *P* with a bulb aspirator, stopcock *Q* being open and stopcock *R* closed.

In the dehydration of the lower alcohols (ethyl, propyl, and butyl) the gaseous olefin passes out at *P*, water and undecomposed alcohol collecting in receiver *O*, whereas in the case of higher alcohols such as amyl, liquid olefin also condenses in the receiver.

This apparatus can be used for any catalytic reaction in which a vaporized liquid is passed over a solid catalyst at approximately atmospheric pressure—dehydrogenation, dehydration, dehalogenation, etc. Also by the addition of a gas inlet tube at *I*, catalytic reactions can be run in the presence of a gas—oxidation, halogenation, hydrogenation, hydration, etc.

Literature Cited

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(2) Vaughen, Ind. Eng. Chem., Anal. Ed., 4, 346 (1932).

Received March 26, 1934.

Thiocyanogen Number

William J. Wiley and Augustus H. Gill, Massachusetts Institute of Technology, Cambridge, Mass.

The thiocyanogen number is a very useful method of determining the composition of oleaginous bodies having oleic and linoleic acids or glycerides as constituents.[1] With tests conducted according to the customary procedure, however, it seems to be subject to considerable inaccuracy.

The usual method of analysis requires 25 cc. of thiocyanogen solution equivalent to 25 cc. of 0.1 *N* thiosulfate and 0.2 gram of the oil to be analyzed. Since there must be a 50 per cent excess, only 12.5 cc. are used in the reaction. In the analysis for the iodine number the 25 cc. of Hanus iodine solution are equivalent to approximately 50 cc. of 0.1 *N* thiosulfate. It is apparent, therefore, that the accuracy of the thiocyanogen number is much less than that of the iodine number, when 25 cc. of solution and 0.2 gram are used in the analysis. In order to make the thiocyanogen number as accurate as the iodine number, as it should be, since it must be in conjunction with the iodine number in these analyses, it appears that samples of double in size should be used.

In order to determine the effect of a larger sample, five different samples of olive oil were analyzed with 0.2 gram of sample and 25 cc. of solution and with 0.4 gram and 50 cc. of solution. In both cases, the thiocyanogen solution was added from pipets having glass stopcocks on the outlets, in order to give greater accuracy than could be secured from a buret.

Table I. Results of Thiocyanogen Analyses

Sample 1	2	3	4	5
		0.2 gram 25 cc. used		
78.05	77.07	74.72	72.78	73.17
77.32	76.55	73.21	71.49	73.42
77.36	77.41	72.92	72.63	72.62
74.00	75.98	67.59	74.46	78.36
73.89	73.52	68.11	74.80	82.97
		0.4 gram 50 cc. used		
75.84	75.21	75.49	73.00	75.58
76.28	75.37	75.73	74.60	75.53
75.63	75.69	76.00	74.39	...

A very wide disparity was encountered in the 0.2-gram sample analyses—a difference which is much greater than would ever be secured in an iodine number. It is obvious that these analyses would lead to very inaccurate results in the linoleic and oleic acid determinations since the error is so great. With the 0.4-gram sample and 50 cc. of thiocyanogen solution excellent checks were secured. With the exception of the first analysis of sample 4, all were well within the limits of accuracy of the iodine determination.

It is therefore recommended that the determination of the thiocyanogen number should be made with 0.4-gram sample and 50 cc. of thiocyanogen solution.

Received March 20, 1934.

[1] Jamieson, G. S., "Vegetable Fats and Oils," p. 345, Chemical Catalog Co., N. Y., 1932.

Solution of Difficultly Soluble Copper Ores

T. H. Whitehead, University of Georgia, Athens, Ga.

It has been known since the time of Fresenius that sulfide ores of copper may often be extremely difficult to get into solution for analysis. When treatment with mineral acids and ordinary aqua regia fails to effect solution, the author has found that the acid mixture recommended by Bonilla (*1*) for dissolving nickel metals is very effective. This mixture consists of 40 volumes of 15 *M* nitric acid and 3 volumes of 12 *M* hydrochloric acid. Samples of ore from 0.150 to 3.0 grams are usually dissolved by 43 cc. of the mixture, after boiling for half an hour.

The excess nitric and hydrochloric acids are easily removed by adding 20 cc. of 18 *M* sulfuric acid after the above treatment and heating until the total volume is reduced to 10 cc. This solution can then be diluted with water and the copper determined either iodometrically or electrolytically according to standard procedures.

Literature Cited

(1) Bonilla, C. F., Ind. Eng. Chem., Anal. Ed., 4, 128 (1932).

Received June 8, 1934

A New Distillation Trap

O. S. Rask, E. Kaplan, Department of Biochemistry, The Johns Hopkins University, Baltimore, Md., and H. C. Waterman, U. S. Department of Agriculture, Washington, D. C.

Among the common laboratory manipulations none can be more troublesome than distillations of foaming and bumping liquids, especially under reduced pressures which fluctuate. To overcome these troubles, various and familar distillation flasks, bulbs, traps, and columns have been devised. Few of these have the desired combination of durability, simplicity in design, efficiency of operation, and general utility, which have been combined in a fairly satisfactory way in the distillation trap illustrated. It is easily constructed and functions very satisfactorily even under a fluctuating house vacuum, in distillations of either foaming or bumping liquids filling the distilling flask into the neck.

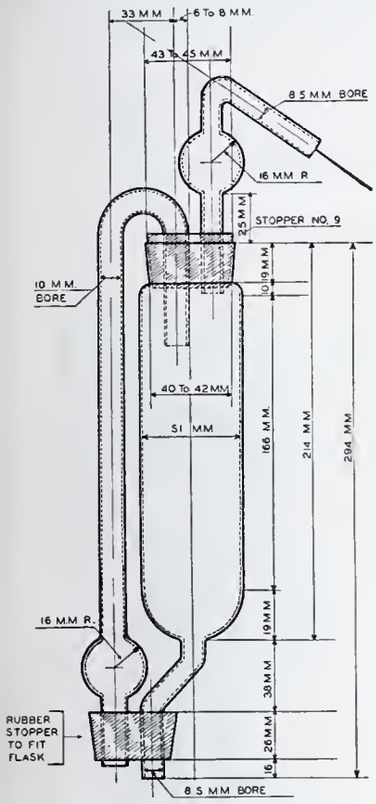

Figure 1. Distillation Trap

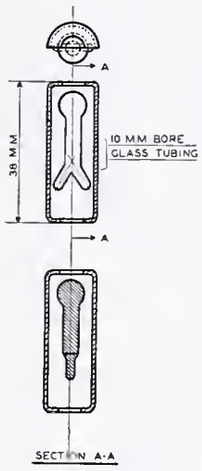

Figure 2. Valve

The valve illustrated by Figure 2, attached by means of fusion or a short piece of rubber tubing to the drain tube of the large safety reservoir, prevents liquids in the distillation flask from ascending into the safety reservoir but allows liquids to drain out of the reservoir and back into the distillation flask.

If desired, the lower bulb identified by dimension 16 M. M. R. in Figure 1 may be omitted without impairing seriously the operation of the trap.

The dimensions specified are those of a trap suitable for a 1- or 2-liter ring-neck flask, and should be increased by 25 to 50 per cent for traps to be used on 3- to 5-liter flasks and probably doubled for traps to be used on 10-liter or larger flasks.

Received April 11, 1934.

Superiodized Sea Water containing more than 500 mg. of iodine in salt form per liter is reported to be obtained by use of a recently patented French process (French Patent 763,083). Iodine-saturated air is continuously pumped into a sea water reservoir stocked with certain marine animals and plants, and through this medium the iodine eventually finds its way into solution in salt form.

A Microburet

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In the practice of quantitative spectrographic analysis in this laboratory, it is necessary to measure small volumes of many different solutions with precision and rapidity (*1, 2*). In the course of routine analytical work, from one to four 0.1-cc. portions of fifty or more different solutions are measured daily. The use of one of the usual forms of microburet or fractional cubic centimeter pipet would require a clean buret or pipet each time a different solution is to be measured. To overcome this difficulty a microburet was designed in which the calibrated portion could be used over and over again without cleaning.

Description of Microburet

Figures 1 and 2 are photographs of the microburet.

Tube *A* is a capillary measuring pipet of 2 cc. capacity, graduated in tenths of a cubic centimeter, each marking encircling the tube and being separated from adjacent graduations by about 0.375 inch (0.94 cm.). The tip end, *B*, of the measuring pipet is attached with a rubber tube to the S-shaped glass tube, *C*. At *D* is attached the delivering tube, *E*, which is a glass tube of 7 mm. outside diameter and 6 inches (15 cm.) long, with its lower end drawn to a tip. The liquid to be measured is drawn into and delivered from this tube, a clean tube being used for each liquid. The tubes are readily removed by detaching them from the rubber tubing connector, *D*, and the bronze spring clip, *F*. Water (tinted with a few drops of red ink) is introduced into the right-hand half of *C* and into the calibrated tube in approximate amount indicated by the levels at *G* and *H*. Level *H* is controlled by varying the position of the top of the air column above it.

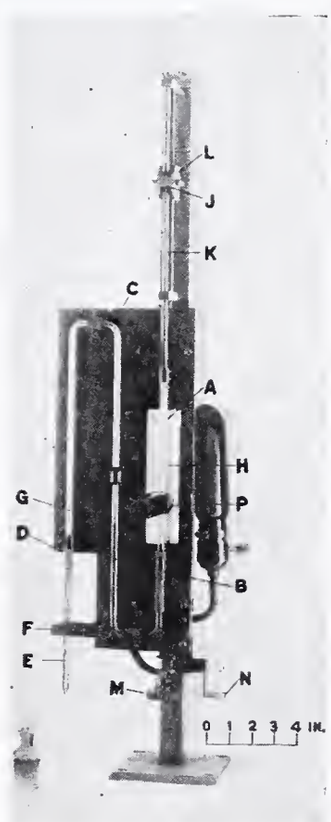

Figure 1

Figure 2

This is done by varying the position of the roller, *J*, which is arranged to pinch the rubber tube, *K*, against a backing plate at any point, maintaining an air-tight seal continuously. The roller is mounted on a carriage, *L*, actuated parallel to the rubber tube by a long vertically mounted screw, the latter being rotated

by hand at M or N. The carriage is designed so that it may be disengaged from the screw for a rapid change of position, the screw being intended for a fine adjustment of the position of the roller.

Tube K should be of semi-transparent pure gum rubber, other types of tubing giving trouble due to air leakage at the point of pinch by the roller. The tubing is kept under slight tension in order to enable the roller to move smoothly and produce definite displacements of the water in the graduated tube.

In use the liquid to be measured is drawn into the delivery tube by dipping the tip of the latter into the liquid and moving the roller upward. When a sufficient quantity has been drawn into the tube the roller is moved downward until the level of the water in the calibrated tube is at one of the graduations. The solution adhering to the tip of the delivery tube is touched off, after which the microburet is ready for use. The desired amount of solution is delivered by running the roller downward, the amount of solution delivered being equal[1] to the volume displacement of the water in the calibrated tube. Precise setting of the level of water in the graduated tube is facilitated by the magnifier, P, and parallax is avoided by the fact that the graduations completely encircle the tube. The measuring tube is viewed against an illuminated ground glass, as indicated.

Literature Cited

(1) Nitchie, C. C., Ind. Eng. Chem., Anal. Ed., 1, 1–18 (1929).
(2) Nitchie, C. C., and Standen, G. W., *Ibid.*, 4, 182 (1932).

Received March 1, 1934.

[1] This is not exactly true, inasmuch as the volume of the air column between the liquid in E and the water in C is not constant but varies with the height of the column of liquid retained in E. Calculation shows, however, that the error in delivering each 0.1 cc. from a 5-mm. inside diameter delivery tube is only about 0.00005 cc. from this source.

Automatic All-Glass Extractors for the Laboratory

W. A. La Lande, Jr., and E. C. Wagner, University of Pennsylvania, Philadelphia, Pa.

The extractors shown in Figures 1 and 2 are designed for extractions with immiscible solvents lighter than water. They are self-contained and compact, occupying little table space as they have a minimum of lateral extension. The absence of projecting parts decreases the liability to breakage. Obviously these extractors can be made only by a glass blower, but it may be assumed that apparatus of such permanent usefulness need not be considered an extravagance because it cannot be homemade.

The extractors are made wholly of Pyrex glass and may be of any convenient size; those now in service have about 1000 cc. capacity to the overflow at level b. Dimensions of parts can be varied within reasonable limits, depending upon the size of the apparatus; hence no dimensions are indicated in the figures, which are drawn to scale.

The liquid to be extracted is poured through G into the main vessel, C, to level a. The solvent is put into the boiling flask, A, and enough is added through G to form a floating layer, ab. The inner tube, B, is of sufficiently large bore to accommodate both the ascending solvent vapor and the overflowing solvent from the upper layer. The solvent vapor passes upward through the ports at D and into the condenser. As the entire path of the vapor is within the extractor, which is thereby kept somewhat warm, there is avoided much of the useless refluxing which occurs when an external tube is used to convey the solvent vapor from boiling flask to condenser. The reflux from the condenser is directed by F so that it passes through the tube E, entering the lower part of the liquid through e, whence it rises through the liquid, eventually overflows through B, and returns to the boiling flask. Tube E must be long enough above the overflow level so that with a light solvent and a heavy liquid a sufficient head of solvent can collect in E to expel it rapidly at e.

The extractor shown in Figure 1 has tube E divided into four branches, the refluxed solvent being thus delivered through the perforated bulbs at four points in the lowermost level of the liquid. The apparatus shown in Figure 2 is provided with a mechanical stirrer and liquid seal. The stirrer is so placed that the upper paddle is in the solvent layer, ab, and the other paddles in the lower liquid. Further, the upper paddle and the lower paddles are opposed so that, by operating the stirrer at moderate speed, the upper solvent layer is pushed downward and the lower liquid upward, the sliding interface and the continuous movement within both layers increasing the rapidity and thoroughness of the extraction. The drainage tube, H, permits the apparatus to be emptied while assembled.

These extractors once started require no attention and can be operated at a high rate of solvent flow. Those now in use are of substantial construction, and are the work of J. D. Graham, University of Pennsylvania glass blower.

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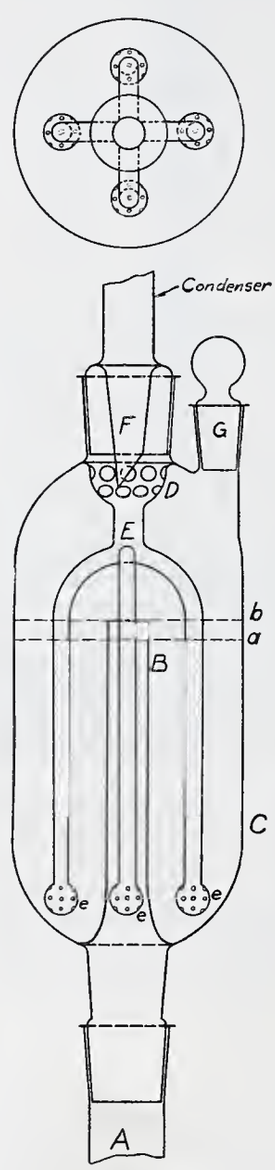

Figure 1

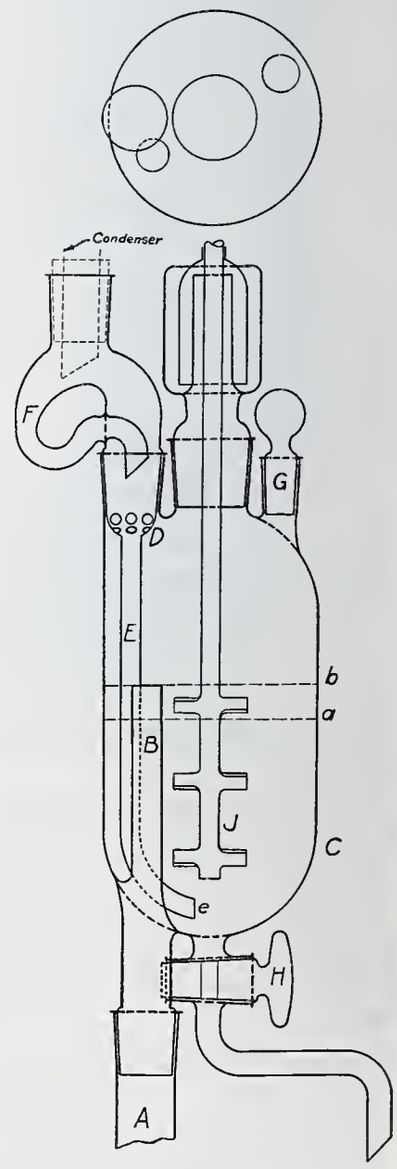

Figure 2

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Measurement of Quality in Rubber Goods by Physical Tests

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Physical tests of rubber products may be classed in two groups—those which measure fundamental physical properties and those which determine service value. Performance tests of the latter class present many difficulties in their proper design and in the interpretation and correlation of the results. Often the value of a performance test is lost because of careless and incomplete mechanical analysis of the factors involved in the test and in the service of the article. Some of these factors are discussed and a number of performance tests are described. Data are presented showing the effect of the dual plastic and elastic nature of vulcanized rubber on the testing of indentation hardness. A time study is given of actual rate of stretching dumb-bell specimens in standard tensile testing.

THE expression "measurement of quality" as applied to rubber goods seems at first thought to be quite definite; unfortunately, it conveys to different persons widely divergent ideas. Engineers in dealing with various materials often interpret the word "quality" as being synonymous with strength. Such usage is quite common in the rubber industry, and stocks possessing high tensile strength may be designated as high quality. A rubber compounder, on the other hand, may consider the quality of a rubber compound to be related to the percentage of pure rubber contained in the mixture. Thus, compounds having only small amounts of other materials added to the rubber would be considered high grade though they might be inferior in strength. Purchasers of rubber products have in the past shared both of these viewpoints, but today the more enlightened consumers understand the expression "high quality" to indicate the relative excellence of an article in performance of the intended service. This seems a more rational interpretation since, in the last analysis, satisfactory service is the prime objective and may or may not be affected by either great strength or high rubber content.

While quality of rubber articles in terms of strength or rubber content is comparatively easy to measure in the laboratory, and fairly satisfactory methods have long been more or less standardized, adequate laboratory evaluation of service behavior is quite another matter. Definition of quality on the basis of performance in service has therefore necessitated the development of new test methods. The older tests for particular properties which are still indispensable for the control of uniformity have been supplanted in product evaluation to a considerable degree by tests directly related to the service conditions. Just as the varieties of articles and types of service cover a tremendous field, so too these performance tests are exceedingly diverse and may be quite simple for some products or highly specialized and complex for others. Some rubber articles are really structures requiring as complicated engineering as the building of a skyscraper, and the play of forces within them in service may be more complex and less capable of complete analysis than the stresses in the skyscraper. Testing such products involves more than merely the measurement of quality of the rubber compounds. Careful and complete analysis of both the structure and the service is necessary, after which development of a suitable test is worthy of the very best engineering thought.

TYPES OF PHYSICAL TESTS

The physical tests ordinarily made on rubber products may be considered as being in one of two classes, the first consisting of those which are designed to measure fundamental physical properties, and the second, those tests which aim to determine service value. Obviously no such classification can be rigid, for in many cases a certain particular physical property may govern the fitness of an article for service. The first class would include measurement of dimensions, of specific gravity, of tensile strength and ultimate elongation or the stress-strain relationship, of compressive strength and the relation between load and deflection, of hardness and resilience, of permanent set, color, dielectric strength, coefficient of friction, and the like. In the second class would be included tests for aging, adhesion, resistance to abrasive wear including tearing and cutting, fatigue tests of various kinds involving repeated applications of stress producing either extension, compression, or flexure, as well as a countless variety of service tests which represent attempts to imitate the actual service under laboratory conditions in such a way that accelerated results may be secured.

The need for laboratory tests capable of giving information rapidly from which the behavior in service of rubber articles

can be reliably predicted and the difficulties which have arisen in such use of present tests have been frequently emphasized. Bierer and Davis (*1*) pointed out the failure of tests of the first class to fulfill the requirements of purchase specifications and discussed the value of performance tests in this connection. They dealt particularly with the various tests for abrasive wear, accelerated aging tests, and a flexing test. While the weaknesses of these performance tests are fully appreciated, they are nevertheless considered to represent advance over the older tests. Dinsmore (*2*) has given a number of instructive examples showing the inadequacy and unreliability of the usual laboratory methods for the prediction of service performance. He selected stress-strain data, abrasion test results, and certain flexing tests, and referred to aging tests although various other tests might also, as he observed, have been included. He cited the variety of performance testing devices which have been developed in recent years as evidence that the need for better tests is well recognized and pointed out that such modifications as the work of Somerville and Russell (*6*) on testing rubber at higher temperatures and that of Somerville, Ball, and Edland (*5*) on autographic stress-strain curves of rubber at low elongations, are steps in the right direction. Dinsmore further suggests that, since rubber is partly plastic and partly elastic slow deformation emphasizes its plastic properties while fast deformation develops more elasticity. High temperatures appear to increase the plasticity effect at slow speed and elasticity effect at higher speeds. Degree of vulcanization is also an important factor. He considers it likely that this dual nature of rubber is important in many tests, mentioning particularly stress-strain, fatigue, adhesion, and possibly abrasion. Finally, he expresses another thought which seems especially worthy of elaboration and emphasis: "More effective laboratory methods may result from careful mechanical analysis of the behavior of rubber products in service. Rubber chemists have naturally failed to appreciate the full value of mechanical studies but they must turn to the physicist for aid in their difficulties. A sound theoretical basis may serve materially to shorten the tedious search for laboratory and service correlation. Certainly the haphazard development of new tests must lead but slowly to progress."

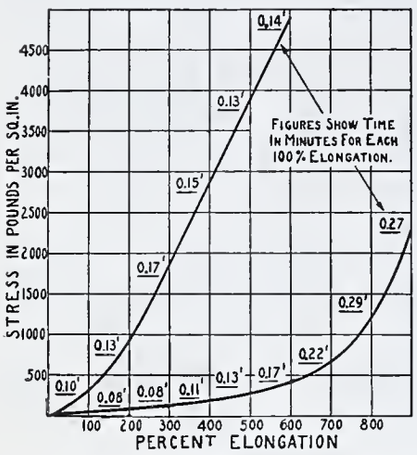


FIGURE 1. RATE OF STRETCHING OF DUMB-BELL SPECIMENS BETWEEN ONE-INCH BENCH MARKS

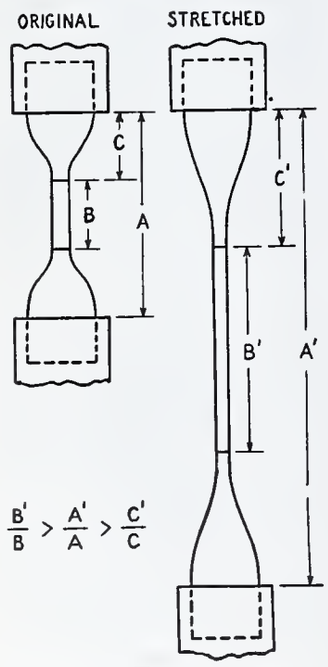


FIGURE 2. EFFECT OF DUMB-BELL ENDS ON RATE OF STRETCHING BETWEEN MARKS

It would ordinarily be supposed that the oldest tests used for rubber products would have been thoroughly investigated and completely analyzed from a mechanical point of view. Two of these tests which were probably carried over from the field of the testing of metals are the measurement of tensile strength and elongation and the determination of hardness. Both of these have been used for more than a quarter of a century by rubber men and have been studied extensively. The lack of completeness of these studies can be illustrated by some data which were recently secured. In measuring tensile strength and elongation, it has usually been agreed that either a uniform rate of application of load or a uniform rate of stretching is desirable for producing duplicable test conditions. Since machines for applying load uniformly would be considerably more complicated than those designed for uniform rate of jaw separation, the latter have quite generally been used. How serious any departure from uniform loading or uniform stretching might be in its effect on the final results is irrelevant in connection with the present question of mechanical analysis. Presumably, the tensile testing machines were intended to give uniform stretching since care has been taken in all specifications to require a uniform and standard rate of jaw separation. A study was made of the actual rate of the stretching of dumb-bell rubber samples between one-inch bench marks when tested in a type L-6 Scott tester. The machine was first carefully checked under load to be certain that the speed of lower jaw travel was uniform and independent of load. Stop-watch measurements of the time required for each 100 per cent elongation between the marks were made by two observers. The data are shown in Figure 1. The time for 100 per cent increments of extension between the bench marks is not uniform for a high-rubber stock having low modulus but increases from 0.08 minute at the start to a maximum of 0.29 minute. In the case of a high-modulus tread stock, the rate is very much more uniform. Evidently, then, the rate of elongation measured with bench marks and dumb-bell samples is influenced by the modulus of the sample. It is believed that the explanation rests in the stretching of the enlarged ends outside of the bench marks. When under sufficient stress these also yield, relieving the elongation of the portion between the marks. This effect is illustrated in Figure 2. While A increases to A', B and C do not increase to B' and C' in the same ratio, and the extension of C lowers the rate of extension of B.

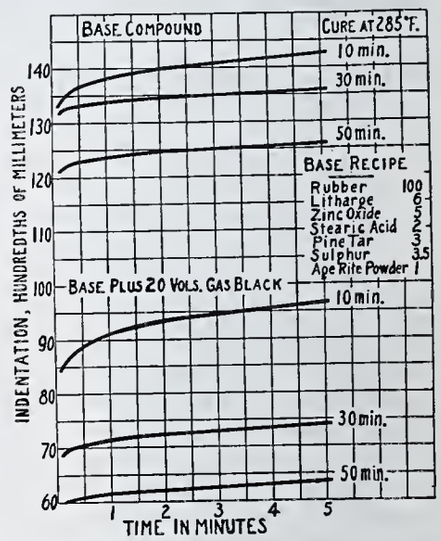


FIGURE 3. EFFECT OF DURATION OF LOADING ON INDENTATION HARDNESS

(Pusey and Jones plastometer)

A simple study of two instruments for measuring indentation hardness again illustrates the lack of complete analysis in the case of even this very old test. It also adds weight to Dinsmore's view of the importance of the dual plastic and elastic nature of vulcanized rubber. Differences in relative

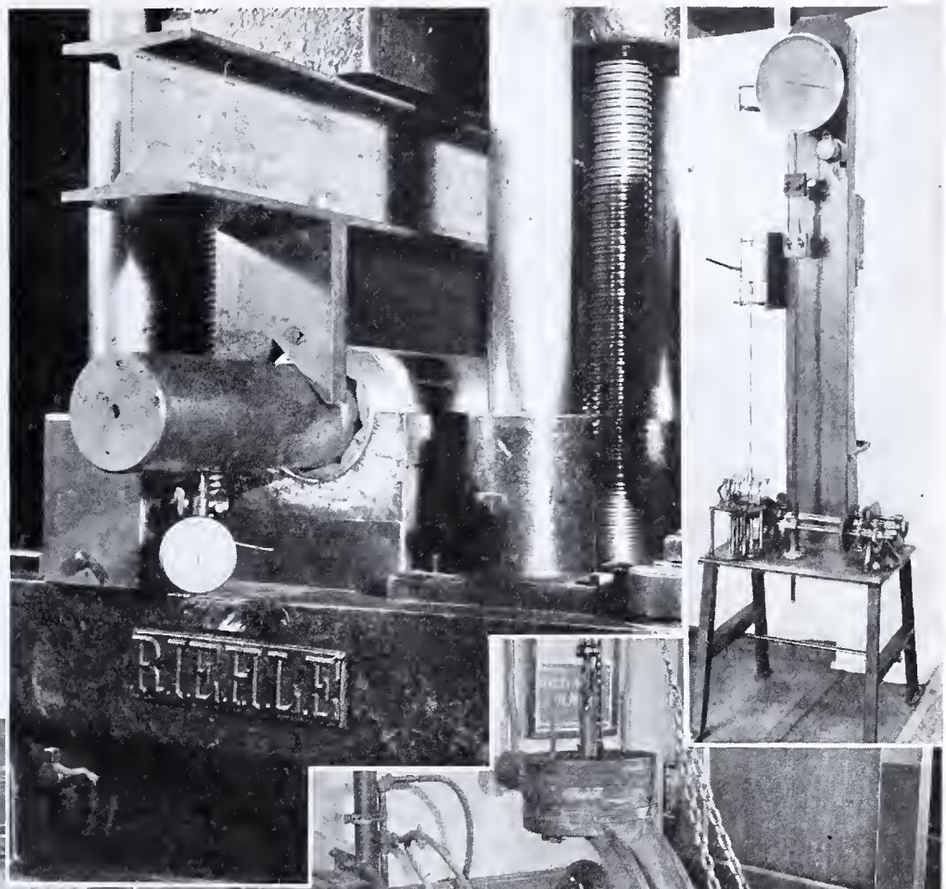
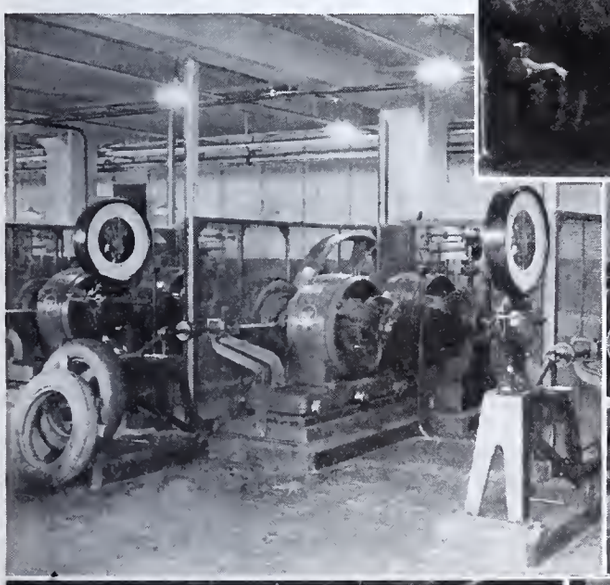
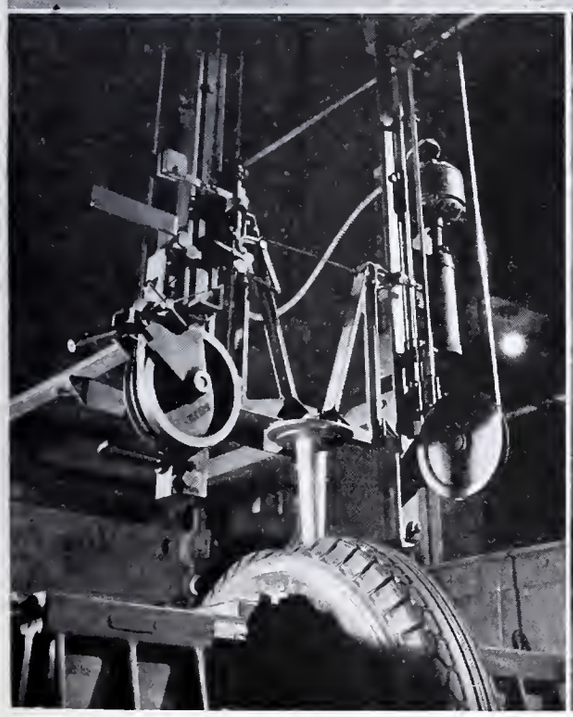


Figure 4 (Right-Hand Corner). Autographic Machine for Measuring Adhesion

Figure 5 (Top Center). Compression-Deflection Test of a Rubber Bearing

Figure 6 (Right Center). Laboratory Test of Tread Wear





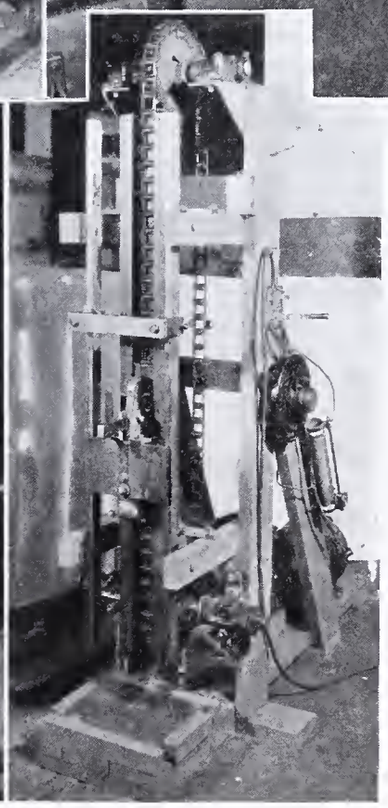


Figure 7 (Left Center). Sprague Dynamometer for Tire Testing

Figure 8 (Left-Hand Corner). "Guillotine" Test of a Tire

Figure 9 (Bottom Center). Drop Hammer for Impact Tests

hardness values were noted in an investigation of certain compounds when using the Shore durometer and the A. S. T. M. hardness tester. The results with three of these compounds are shown in Table I. It must be remembered that, in the A. S. T. M. instrument, the indenting point operates under a dead-weight load, and readings are not taken until after at least 30 seconds of weight application. The durometer, on the other hand, is a spring instrument, and the quickest possible and highest reading is taken. The scales of the two instruments read in reverse; that is, the higher durometer readings represent harder stock while the higher readings of the A. S. T. M. instrument show softer stock. Thus, the results on the 30-minute cures using the A. S. T. M. test show stocks A and B to be of substantially the same hardness while stock C appears decidedly more hard. The durometer test, however, indicates that stocks B and C are of the same hardness and that both are harder than stock A. If we bear in mind that undercures, such as the 30-minute cure of stock B, should be more plastic than correct or overcures, such as those of stocks C and A, the differences with the two instruments can be readily explained on the basis of plastic flow of stock B which affects the A. S. T. M. measurement but not the durometer reading. This is confirmed by the readings at the best cures. A further check (*8*) was made using a high-rubber stock and a 20-volume gas black compound in three cures, measuring hardness with a Pusey and Jones plastometer which is also a dead-weight indentation instrument. Readings were taken over a somewhat extended period. The results are shown in Figure 3. The curves for the undercured stocks (10 minutes at 285° F.) show plainly the effect of plastic flow, some of which persists even in the overcures (50 minutes at 285° F.) as shown by the slopes of these curves. Hardness of vulcanized rubber compounds thus appears to consist of two parts, one of which is due to resistance to resilient deformation and the other to resistance to plastic deformation. Some methods of measurement include both in the indentation hardness result, and other methods show only the resilient hardness depending on the duration of the application of the load.

Table I. Comparison of A. S. T. M. and Durometer Hardness

Stock	Best Cure at 280° F.	Samples at Best Cure: Tensile strength	Ultimate elongation	Modulus at 300% elongation	A. S. T. M. hardness	Durometer hardness	Cure, 30 min. at 280° F.: A. S. T. M. hardness	Durometer hardness	Permanent set, stretched[a]
	Min.	*Lb./sq. in.*	%	*Lb./sq. in.*					
A[b]	15	2650	660	600	125	39	78	50	34
B[c]	45	1570	400	950	69	59	75	57	60
C[d]	30	1070	425	650	69	56	65	58	25

[a] 80 per cent of ultimate.
[b] Stock A (parts by weight): rubber, 36.5; inner tube reclaim, 36.5; zinc oxide, 6.5; mineral rubber, 11.0; palm oil, 1.3; sulfur, 3.2; accelerator, 5.0; total, 100.0.
[c] Stock B: 100 parts A + 82.5 Georgia clay.
[d] Stock C: 100 parts A + 82.5 Missouri clay.

The significance of this kind of analysis in making possible better correlation with service has been intentionally omitted from the discussion because much more work will be necessary before it can be fully evaluated. Surely, however, such analysis cannot help but give us better appreciation of the value of the tests which are made and a more accurate understanding of how to use the test data. We must not fail to realize the indirect nature of all laboratory tests nor should we underestimate their value for comparative purposes, even though direct correlation with service is not always clear. Certainly, direct interpretation in terms of service value is not possible for tests such as determinations of stress-strain relationships, permanent set, and adhesion, except in some special instances. Yet, what rubber technologist would be willing to have such useful tools taken from him and would be content to rely on imitations of service and on simple hand tests alone? Service evaluation or prediction represents a judgment on the part of the technologist, and all of the information possible, comparative and indirect, as well as direct data, must be assembled if the final estimate is to be a good one.

Difficulties in Correlating Laboratory and Service Results

The difficulties which are experienced in correlating laboratory test results with service performance must be attributed to one or both of two causes. Either the tests themselves are improperly designed or the results secured from the tests are not correctly interpreted. Improper design is a frequent consequence of hasty, unsound analysis of the service which fails to give full knowledge and appreciation of all the conditions and forces that are involved. A fundamental requirement of good testing is that the service to be measured shall be first completely and accurately defined before attempting the design of a test. A good example of the lack of such definition is found in the case of abrasive wear, particularly as applied to tread wear of tires. The various conditions and forces involved are so numerous and complex that we frankly admit our shortcomings in respect to their analysis. Yet we attempt to design laboratory abrasion tests and we carry on extensive road testing at enormous expense without really knowing what it is we are trying to measure. Possibly more time and money spent in determining just what road wear consists of and in establishing the relative importance of the various service factors might pay more dividends in the end than all of these expensive test programs. Proof of the serious inadequacy of present analyses of road wear factors is evidenced by the difficulties which different tire manufacturers have in checking one another's road tests, and by the fact that each manufacturer has elaborate sets of road test data which show that his tires are the best of all competitive brands. It is worthy of note that laboratory abrasion tests do correlate fairly well with service wear when the latter is simple enough to be readily analyzed or capable of being closely duplicated under laboratory conditions.

Improper design of laboratory tests may result also from failure to carry over into the test apparatus a proper balance of the conditions and forces known to exist in the service. This is often caused by the necessity of accelerating the investigation. Performance tests would fall short of their purpose if they required as long a time as the service life of the article. The acceleration of failure is secured usually in one or more of the following ways: (1) by increasing the severity and intensity of forces on the sample (higher pressures or loads, harsher abrasive surfaces, etc.); (2) by increasing the temperature; and (3) by increasing speeds. Through emphasizing certain of these individual factors, the normal balance of service conditions may be upset, both directly and, as is often not realized, indirectly, since change in one condition may cause resultant changes in others. Obviously, without such emphasis the test would not be accelerated. If the emphasized conditions are those which are principally responsible for the ultimate failure of the article and if the other factors which are involved are not important in contributing to the cause of failure even though they may be indirectly affected, reasonable success may be anticipated with respect to correlation of such tests with

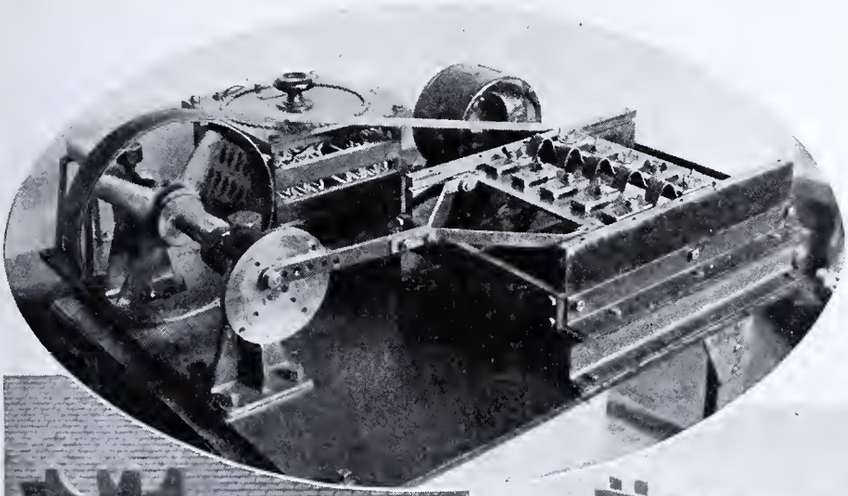
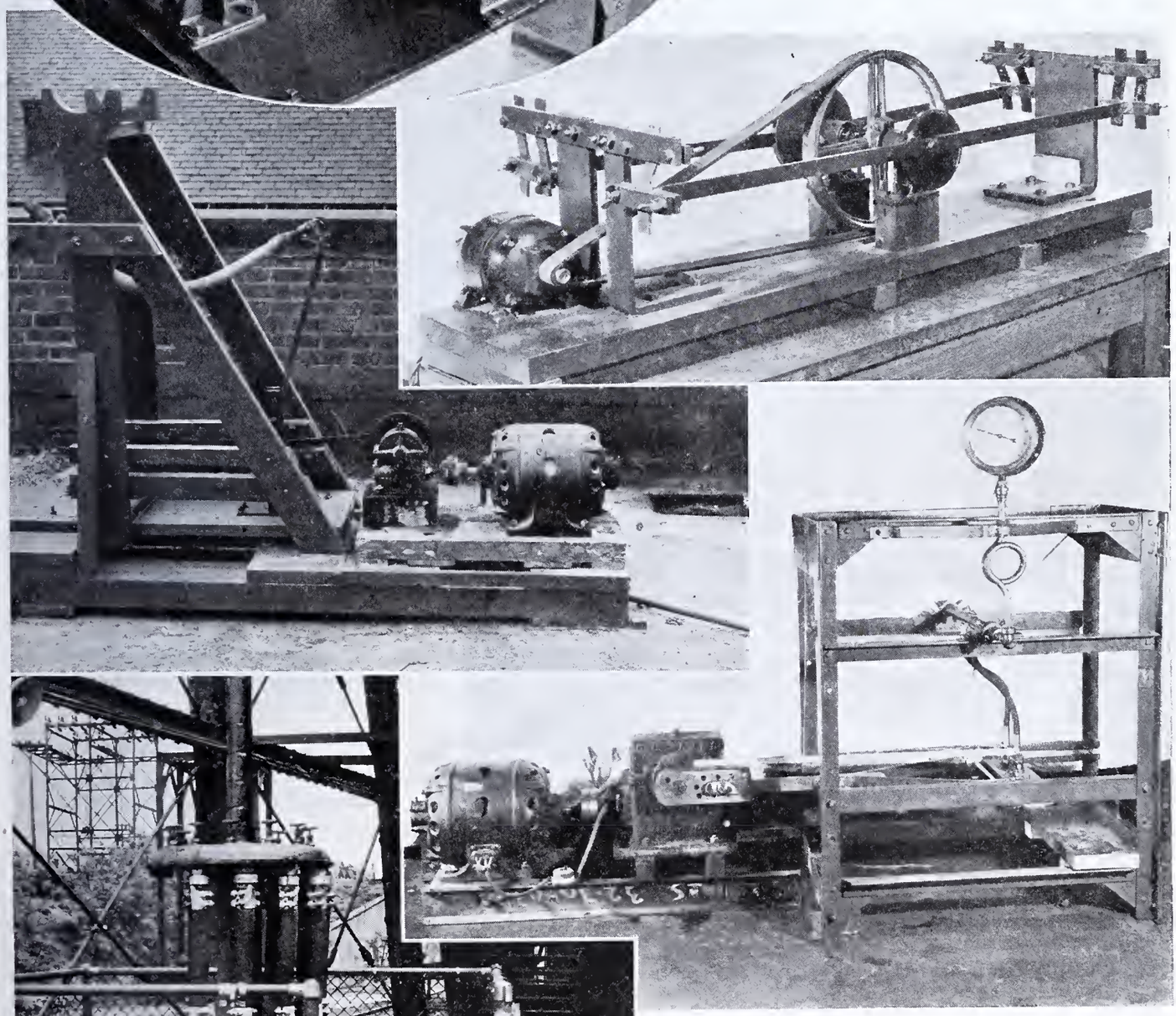


Figure 10 (Left). Fatigue Testing in Flexure

Figure 11 (Below). Flexing Test for Soling



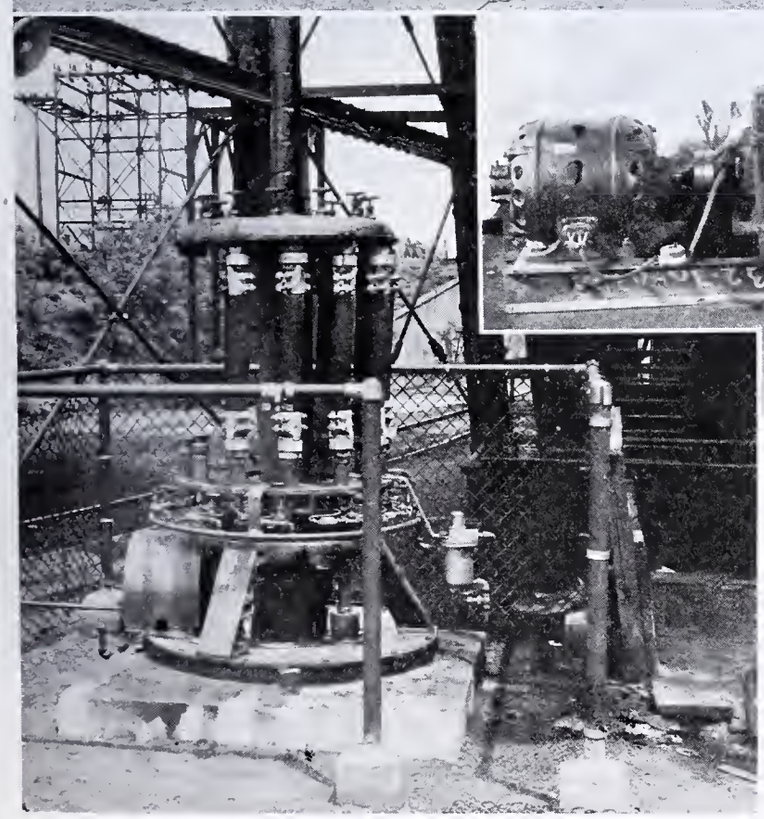


Figure 12 (Left Center). Flexing Test of Gasoline Hose While Containing Liquid

Figure 13 (Above). Flexing Test of Grease-Gun Hose under 2500 Pounds per Square Inch Grease Pressure

Figure 14 (Left). Performance Testing of Steam-Hose Torsional Flexing under 250 Pounds per Square Inch Steam Pressure

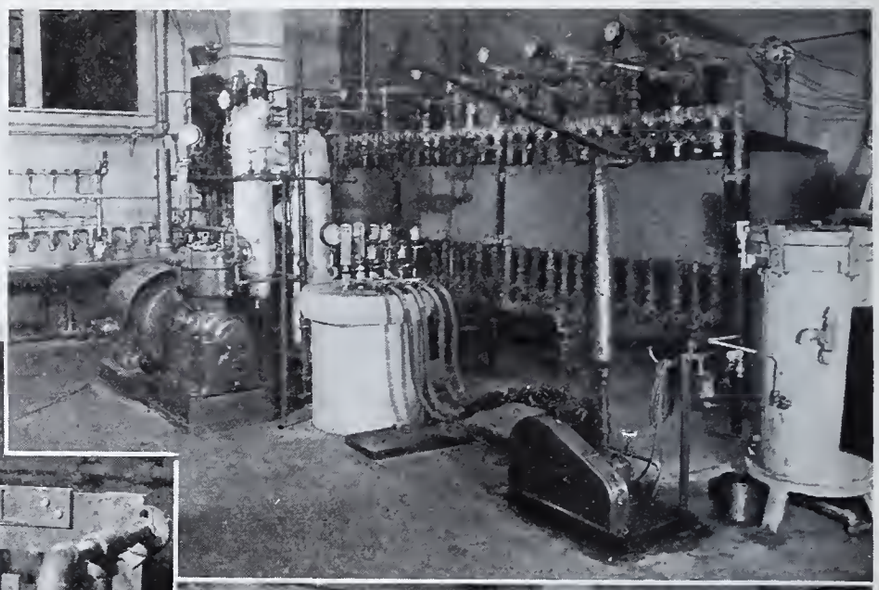
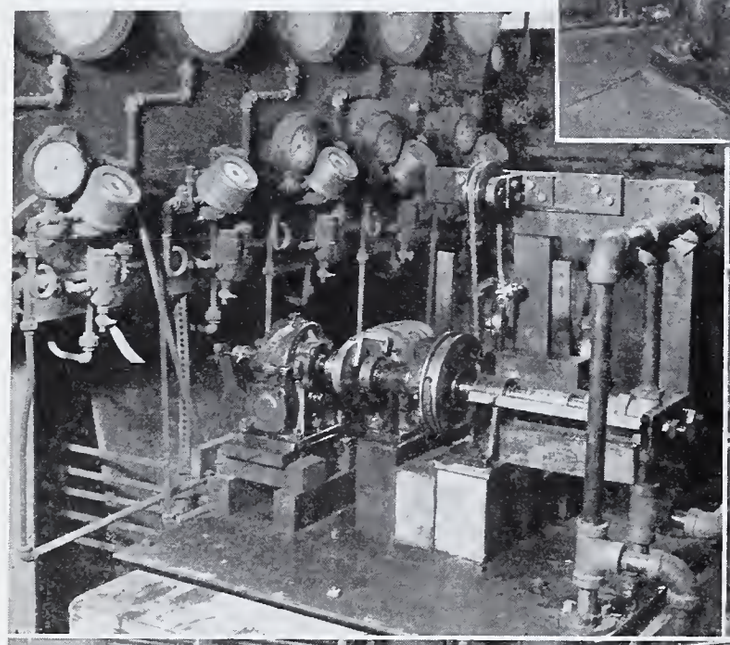
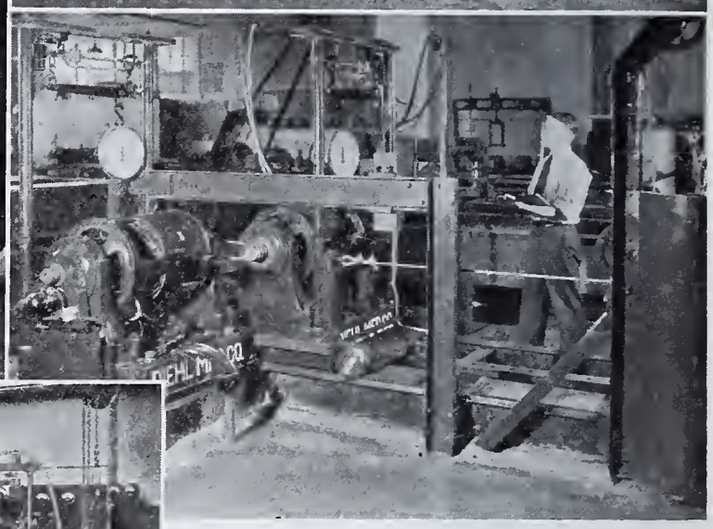


Figure 15 (Right). Comparative Performance Test of Pneumatic Tool Hose

Figure 16 (Below). Performance Test of Steam Valve Disks





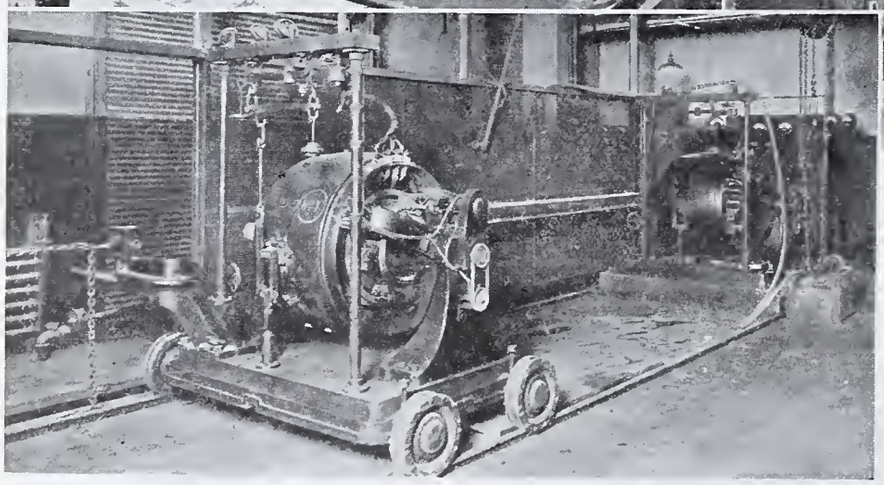


Figure 17 (Above). High-Speed, 25-Horsepower Dynamometer for Testing Small Belts

Figure 18 (Left). One-Hundred-Horsepower Sprague Dynamometer for Testing Power-Transmission Belting

service. On the other hand, when the balance of the service factors is seriously disturbed in the test conditions, it is unlikely that good correlation can be obtained. The only alternative which remains then is to analyze the service completely and emphasize all factors in the same proportion.

In regard to interpretation of laboratory tests, it is not infrequent that attempts are made to apply test data to services that involve differences in conditions which are significant but not fully appreciated. Here, again, the solution of the difficulties which arise must reside in more careful analysis of both the test and the service. It is also quite usual to encounter lack of understanding of the limits in precision of engineering data secured by test. Almost any of the performance tests serves to eliminate products which are radically unfit for the intended services. It is only when finer distinctions are involved that serious reversals are encountered. For instance, several of the better abrasion resistance tests will distinguish between first grade and second grade treads when the actual service differences in the treads are fairly wide and when the treads have similar degrees of hardness. It is only when close comparisons between treads of dissimilar hardness characteristics are required that serious reversals occur. While such accurate measurement and correlation are extremely desirable and may some day be possible when we have learned to analyze all of the conditions closely enough, it must be admitted that as yet we are somewhat in the position of trying to weigh a dust particle with ordinary counter scales.

Laboratory Tests

Some pictures of laboratory testing which follow are shown, not with any idea that they may serve as shining examples of perfect mechanical analysis or as the last word in quality measurement, but merely that they may be suggestive as to the modern trend of test development and may illustrate the simplicity of the mechanical movements at present utilized in developing performance tests. As has

already been suggested, the details of such tests are extremely varied but the fundamental mechanical principles are not nearly so diverse as appears at first glance. Figure 4 shows a machine test for adhesion or "friction pull." The specimen in this case is a strip of transmission belting one inch in width. This test involves simply the measurement, by means of a pendulum dynamometer head, of the force required to separate plies of the specimen under standardized conditions. As has been frequently pointed out in the literature, the correlation of such tests as this with service performance is extremely unsatisfactory. Figure 5, however, shows a test in which the service correlation is very positive. In this case the deflection of a rubber bearing is being measured under various compressive loads applied to a shaft by means of a universal testing machine.

As has been suggested, performance tests which appear to be very good imitations of service conditions often fail to give satisfactory service correlation, probably because of failure to include in the test the essential characteristics of the actual service. Figure 6 illustrates such a case. This machine was designed to test tread wear, using as test specimen a small pneumatic tire which is run on a rotating track made of standard road concrete. The test is of the angle-slip type and provision is made for control of the angle. The speed can be varied as well as the dead-weight load supported by the tire. The road wheel is the driven member and in turn, through contact, rotates the tire wheel which is mounted as an idler on ball bearings. The amount of tread wear is measured by accurately calipering the depth of the nonskid grooves. For a time it appeared that this test would correlate very reliably with actual road service, but, as often happens, it was necessary only to continue testing on a sufficient number of tires to encounter serious reversals.

In Figure 7 is shown a view of tire testing on Sprague dynamometers. In such tests a generator is driven by a motor through controlled contact of tire and road wheel. The actual horsepower expended on the road wheel is measured by weighing the generator torque and measuring the speed, using the Prony brake formula for the calculation. These tests have been quite reliably correlated with actual service for the evaluation of tire carcass performance. Figure 8 shows a rather obvious but useful impact test known as the "guillotine test." This has given valuable information concerning the ability of tires to withstand service conditions. In this case the impact member is dropped between guides from controlled heights in an elevator shaft, striking a blow of known force on an inflated full-sized tire, properly mounted.

Another device for impact testing, as shown in Figure 9, has been successfully used for the testing of rubber-covered metal plates, such as are used in lining chutes, grinding mills, etc. In this device a chain elevator raises a 50-pound weight carrying a hemispherical impact surface to a predetermined height at which the weight is tripped from the elevator. The heavy body falling freely between nearly frictionless guides strikes a blow of known force on the specimen placed below on a suitable solid support. A very interesting result was observed with this apparatus while testing sheets of rubber which had been bonded firmly to metal backing (*3*). Certain specimens, when tested dry, required approximately one hundred blows before complete failure, which was taken as the number of impacts necessary to cause the rubber to tear apart sufficiently to expose the metal base. In appearance the failed sample showed a very roughened surface over a circular area of diameter about equal to that of the impact ball. At the center of this area a circular hole of small diameter extended down through the rubber to the metal. When the experiment was repeated, with the difference that the surface of the rubber was kept wet with water, failure took place after three or four blows. Irregular radial cracks extended from the center of percussion outward, and there was no appreciable roughening of the surface. Apparently the water acted as a lubricant, concentrating the full force of the blow at the center of percussion rather than permitting the energy of the blow to be dissipated through a larger volume of rubber by means of friction.

Figures 10 to 14 show applications of flexing tests to various rubber products. Such tests can seldom be correlated directly with service performance, but they are extremely useful for comparative purposes. The machine illustrated in Figure 10 is used with rubber strips or dumbbell specimens and is similar to the DeMattia flexing machine (*4*). A crosshead is driven by an eccentric at controlled variable speed. By using suitable settings of the clamps, it is possible to flex the rubber samples in bending only, as shown, or in extension. In either case the first sign of failure will be the development of small cracks which finally lead to a complete rupture of the specimen. Figure 11 shows a bending fatigue test on soling stock. This differs from the previous test in that the specimens are under slight tension produced by the weight of the driving arms which are supported by the specimens. In Figure 12 the performance relationship is more clearly defined, for in this case a specimen of gasoline hose full of the liquid is bent back and forth until the tube fails and the gasoline penetrates into the body of the hose. Figure 13 shows specimens of grease-gun hose filled with grease under high pressure, which are flexed with a reciprocating motion until failure and consequent release of the pressure take place. Figure 14 shows a recent performance test for steam hose. In this case the lower platform moves with an eccentric motion, causing the lower end of the hose specimen to be rotated in a circle about 4 inches in diameter. During test the hose is subjected to internal steam pressure of 250 pounds per square inch and external action of the weather. It is thus quite typically a performance test imitating actual service conditions as encountered by railway steam hose.

Another performance test, in which a rather elaborate attempt is made to duplicate on a laboratory scale, a complicated set of service conditions, is shown in Figure 15. In this case, service life of four samples of pneumatic tool hose is being compared. The apparatus consists of an air compressor which discharges into a receiver through equipment arranged to give constant temperature and pressure in the receiver. The compressed air from the receiver flows through the hose specimens after having received a known addition of lubricating oil at the receiver outlet. The compressed air is released from the hose through a valve mechanism which duplicates the impulse action of a pneumatic hammer. The test may be accelerated by raising the temperature and pressure of the compressed air. Figure 15 also shows a steam rack and a digester which are used for heat deterioration tests of hose specimens. In Figure 16 equipment for testing steam valve disks is shown. A valve installed in a high-pressure steam line contains the disk under test, and mechanical arrangements are provided whereby the valve is opened by a motor which raises a weight at the same time. The mechanism then trips and the falling weight closes the valve, assuring duplicate force conditions at each closure.

Figures 17 and 18 show dynamometer equipment for testing belts. Both of these sets are so arranged that very complete information can be secured. In each case one dynamo is mounted on a track which permits control and measurement of the total tension on the test belt. In each set both dynamos are cradled and equipped for torque and speed measurement so that the actual pulley horsepowers can be calculated excluding the dynamo losses. In each case one

dynamo operated as a motor drives the other dynamo as a generator through the belt. Knowing the pulley horsepower in each case, the power transmission efficiency is determined. The effective power load can be regulated by means of adjusting known resistances in the generator discharge circuit. With a given total tension on the belt, it is possible to use so much resistance that slippage of the belt occurs as would be evidenced by the readings of the revolution counters on the units. The set shown in Figure 17 was recently designed for testing small V-belts at high speeds. It is capable of being operated continuously at speeds up to 5000 r. p. m. with power loads of 25 horsepower. The set shown in Figure 18, similar to that previously described by Sturtevant (7), is capable of handling 100 horsepower at speeds up to 1800 r. p. m. It is suitable for use with full-size power-transmission belting of either flat or V-type.

It is hoped that this discussion and the illustrations may serve to stimulate ideas and work which will lead to progress in development of well-designed laboratory performance tests and their correlation with service.

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Chemical Studies of Wood Preservation

I. The Problem and Plan of Attack

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The chemical problems involved in wood preservation are discussed with special reference to pressure-treated pine poles. Preservation of wood is achieved by the use of poisons which in reasonable concentration are destructive to a variety of wood-destroying organisms and which must be permanent in the weather. Variability of penetration of preservatives and inequality of their distribution in wood, partly due to Nature's infinite variety, make significant sampling and analysis difficult. Accordingly little quantitative information has been available about the distribution of preservatives and the depletion of toxic value by sun, wind, rain, and soil moisture. Some of the devices and methods which promise to accelerate testing and to supply quantitative data are outlined.

PRESERVED timber has been used in industry for about a hundred years with results so satisfactory as to leave no question as to the economic value of preservative treatment. However, a quantitative measure of this economic advantage and the relative merits of the several kinds of treatment which are available still remain doubtful in many particulars. A constant stream of unanswerable questions is still arising with regard to the quality of creosote oil for preservative purposes and the methods of application of such oils to various kinds of timber, so that a systematic continuing study of the subject is necessary.

Such a study has been under way for many years in the Bell Telephone System and in recent years the volume of useful information on the chemical aspects of the subject has attained considerable proportions. Much of this information is available for publication. In presenting it, however, the authors wish to emphasize that it should be construed as an account of experimental work, the significance of which is left to the judgment of the reader. Although the study has naturally shaped itself around Bell System problems, the experimental methods and results described are not to be regarded as a statement or a forecast of the engineering practices or preferences of the system. These practices are based on a variety of considerations, many of which involve nothing of chemical interest and are accordingly omitted from the present discussion.

It is the purpose of this paper to outline the chemical problem and to state the plan of attack which has been followed. Later papers will deal more in detail with the methods used and with some of the results of the study.

The authors have limited themselves at the outset to a certain well-defined but important area of the field of wood preservation. Because of the preponderating importance of the telephone pole to the industry, attention has been largely confined to it in the present papers. To a great extent the discussion is further limited by excluding from extended consideration those sorts of poles, such as chestnut and cedar, which are not usually economically susceptible to pressure treatment. The depth of sapwood in these species is small; the penetration of preservative beyond the sapwood into the heartwood is very slight; and the heartwood has a greater natural durability than the sapwood. Chestnut and cedar poles are accordingly commonly treated only in the butt section by an open-tank treatment at atmospheric pressure. Such treatments protect the underground section of the pole very materially and are economically valuable. Poles so treated are, however, less well adapted to reveal the full possibilities of wood preservatives than poles of the cheaper, less durable, and more treatable species which have been subjected to full-length pressure treatment.

The principal object of the authors' concern has therefore been pressure-treated Southern pine, a type of timber which has been extending its field of use more and more into areas in the North, East, and Southwest. Other species of treatable timber which come in for incidental consideration in these studies are Douglas fir and lodge-pole pine which have intermediate depths of sapwood. The former is usually subjected to full-length pressure treatment, the latter to open-tank butt treatment.

For similar practical reasons the data to be published largely concern creosote oil as a preservative, although the authors have examined, to a limited extent at least, most other

preservatives which are in use or have been proposed. Creosote oil is the middle cut from the distillation of coal tar, a by-product of the coking of bituminous coal. The processes of coking are and have been for many years undergoing an evolution which reflects itself in the nature of the coal tar produced. Likewise the processes of distillation of the resulting tar have undergone changes from year to year, making for changes in the character of the creosote oil. In general, however, it may be said that creosote oil represents from one-fourth to one-half of the original tar and has a boiling range from about 200° to 360° C. The portions of the tar which are rejected consist of light oils of low boiling point and residual pitches. The creosote oil is a mixture of two or three hundred chemical substances in varying proportions and displaying a variety of physical and physiological properties.

For present purposes, one may think of the process of applying creosote oil to timber as essentially one of driving the oil into the wood by external application of hydraulic pressure, either with or without previous evacuation of the air in the cells of the wood. Numerous variants of the process are in use.

Penetration of Preservative

Even a casual examination of poles treated in this manner reveals facts of fundamental importance in a consideration of the problem of wood preservation, most important of which is that the heartwood is rarely penetrated to any extent. This means that during service we must depend upon the natural durability of the heartwood or upon the continuity of the envelope of treated wood with which it is surrounded.

According to the practice of some years ago, perhaps the majority of the poles in a given cylinder charge were penetrated to the extent of 90 per cent or more of the depth of the sapwood. Some might be penetrated to the extent of only 50 per cent or even less, especially if the sapwood was very deep; some pieces, particularly of shallow sapwood, might be penetrated to the surface of the heart. Substantial progress has been made in recent years in many plants toward securing complete and uniform penetration, but the danger of incomplete penetration is still present and must be constantly combated. In addition, while it often happens that the depth of penetration is approximately uniform on all sides of the pole, not infrequently the penetration is much deeper at some points than others, leaving an untreated core of wood of very irregular cross section.

It is also found that the oil is not evenly distributed throughout the treated portion of the wood. Cases of decay have been discovered which were due to a deficiency in quantity of oil retained in portions of the wood which the oil had actually reached. Often the oil concentration is greater in the outer layers of sapwood, sometimes in the inner; rarely is it uniform within the limits of experimental error of analysis.

The causes of the uncertain and uneven distribution of creosote in wood are somewhat obscure, but are known to involve among other things the moisture content, the thickness of growth rings, the over-all density of the wood, the characteristics of the oil, and the nature of the impregnating process. It is sufficient for present purposes to point out that the creosoter has to deal with a raw material of far more variable character than fabricated material with which manufacturers are commonly concerned and that this variability tends to be reflected in the finished product. The examination of old creosoted poles also reveals that variability of penetration is a factor of prime importance in determining the excellence of the finished material. In the great majority of cases decay occurs sooner or later in the untreated part of the wood.

From the laboratory man's point of view this variability results in an extremely difficult problem of sampling. Indeed, a primary need of the industry today is a simple quantitative measure of the amount and excellence of distribution of preservative in a train load of timber. Accordingly, the problem of sampling poles for analysis will constitute the subject of a later paper.

Service Conditions

In considering the quality of the preservative treatment one must take into account the peculiarities of service conditions. Proper creosoting of ties, piles, cross-arms, or poles calls for adaptation of the treatment to the kind of use to which the timber is to be put. In the case of the pole, the upper part is exposed to sun and wind and the lower part to more or less moist and close-packed earth, at more nearly constant temperature and with little ventilation. Just above the ground line there is a region which is kept continuously moist by capillary flow of water from the earth and is also exposed to the sun and to winds laden with spores of wood-destroying fungi. In general, at least in untreated poles, this region is most subject to decay. Obviously one cannot ignore differences of climate, including rainfall, sunshine, and air temperature as affected by latitude and general topography. Thus a degree of preservation which is quite adequate for the high latitudes of Central Europe may be wholly insufficient for subtropical conditions.

This observation immediately points to the necessity of some means of measuring the permanence of preservatives introduced into the wood and of determining the loss of preservative value. In this connection some quantitative measure of the toxicity of the residual preservative is essential and for this purpose resort must be had to the use of cultures of wood-destroying fungi. These cultures, for the sake of constancy of performance, had best be pure cultures of single organisms and, in order to avoid overlooking specific toxic effects, preservatives need to be tested with several representative organisms. Such tests are subject to the influence of a great many factors and the whole matter will be dealt with at length in later papers.

The merits of a preservative treatment naturally depend not only upon the distribution of the preservative and the influences which tend to deplete the supply of preservative, but also upon the quality of the material which is introduced. Contrary to wide-spread opinion, it is possible to find creosoted timber which has undergone decay within the penetrated part of the wood. With the radical innovations that have taken place in recent years in the processes of creosote oil production, this fact should be recognized as one of outstanding importance. Indeed, the reputation of creosote oil is based principally on the behavior of a product distinctly different (whether better or worse) from that which tends to prevail in the treatment of new timber at the present time in America. The older types of oil are naturally more generally represented in timber which has withstood the test of decades of service.

Interpretation of Test Data

Assuming that one has devised means of sampling and analyzing a lot of timber and of determining the distribution and toxic effectiveness of the preservative in it, there remains the question of how to forecast permanence without waiting many years to observe the behavior of new experimental material. The Bell System is fortunate in having available for examination several millions of poles in all parts of the United States. Information is on record about a considerable number of these poles concerning the kind and quality of oil originally used, the method of treatment, and the age of the specimens. These poles are affording a rich fund of information as the examination of them is extended from year to year.

Particular attention is being paid to poles which have behaved conspicuously well or conspicuously badly in service and a great deal of insight has been gained thereby into the nature of the depletion processes and causes of decay.

The examination of old poles furnishes information primarily with regard to the behavior of poles in the latter part of their life. The known facts about the treatment of these timbers are often insufficient to define their original condition with exactitude. In order to complete the picture, one must know about the behavior of poles in infancy and youth. For this purpose, in common with many other investigators of wood preservatives, the authors have resorted to the use of posts specially treated for the purpose. These are exposed in convenient plots located in different parts of the country in order to observe the effects of climatic influences. The value of this method has been greatly enhanced by analytical examination of the condition of the posts at the outset and from year to year. The trouble with most of the published work about this type of experiment in the past has been that it consisted largely in counting the number of specimens which showed decay after various intervals of time and that the total time elapsed has been insufficient to put the material to a crucial test. By periodic sampling and analysis of such posts the authors have been able for the first time to plot depletion curves which show clearly that the loss of creosote from wood proceeds at an astoundingly large rate during its early years. It dies away later to a slow depletion which may be only roughly extrapolated into the far distant future. However, by piecing together the information secured from old poles in service with that obtained from young ones in test plots the whole process of senescence can now be pictured much more adequately.

After all, we are interested in post-mortem findings primarily in order to protect material which is yet to be manufactured and installed. Still more rapid methods are necessary to secure adequate information about new preservatives or new varieties of creosote if this information is to be of value within the lifetime of the present generation. For this purpose the authors have resorted to small-size specimens, depending on the principle that the ratio of surface to volume must determine in large measure the rate of weathering, and in order to imitate poles, have used sections cut from pine saplings about 15 to 20 mm. in diameter and of length in proportion to that of standard poles. The sapling has a great advantage over a turned stick of wood in that the grain runs parallel to the surface and the structure is otherwise imitative of the full-size pole. Allowance must be made for the fact that the sapling contains little or no heart and therefore is impregnated throughout. Roughly speaking, such saplings have a ratio of surface to volume ten times that of normal size poles and will lose preservatives at correspondingly greater rates.

The authors have considered and to a limited extent experimented with artificial weathering machines for hastening the depletion process in such specimens. However, such devices are somewhat cumbersome and expensive and a considerable uncertainty always remains as to whether the several depletion factors have been accentuated in proper proportion to one another. For this reason this type of device has not been extensively used. It has been found that saplings treated with standard preservatives when exposed to the weather, especially in southern climates, will within a year or two give comparative results which are in harmony with industrial experience in full-size material. The process of treating such small saplings is so expeditious and inexpensive that it has been possible to carry on simultaneously experiments with scores of new preservatives or variations of preservative treatment. With relatively little expenditure of labor, the specimens can be inspected from time to time and first approximations to a reliable prediction of behavior can be made by comparison of the behavior of unknowns with standard materials of well established industrial history.

When one contemplates the necessity for some sort of specification test for the purchase of a complex preservative such as creosote oil, he realizes that a practical test must be completed within a few hours or at most a few days. Such a test cannot be expected to have the finality of an actual exposure test and requires much correlative information for its interpretation. However, it may be briefly stated that the principal cause of depletion of preservative value in creosote oil is evaporation. Accordingly, a useful tool has been developed which measures the rate of evaporation of an oily preservative under conditions which are imitative of those which prevail within the wood structure. The data so obtained about a variety of oils have been correlated in some detail with tests of the identical materials in actual exposure to the weather. The evaporimeter which has been devised also furnishes material for estimation of residual toxicity at various stages of evaporation. An account of this device will constitute the subject matter of an early publication.

The papers which are to appear within the next few months must be regarded as progress reports, since knowledge is not complete at the present time upon any phase of the subject. They are to be published to supplement the experimental work of others and to secure the benefit of critical comment.

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II. Sampling Poles for Chemical Analysis

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In the study of the changes in quantity and quality of preservatives in poles over a period of years, an accurate, convenient, and nondestructive sampling method is required. It should provide a sample suitable for extraction, giving extracts ample for toxicity tests; should leave the pole uninjured with respect to its future behavior as a test specimen or as a pole in service; and should, preferably, permit observation of wood structure, penetration of preservative, etc. Above all, the sample should be accurately representative of the pole as a whole.

The normal distribution of preservative in poles treated by even the most thorough pressure processes is far from ideal. Most timbers used for poles have a well developed heart, or inner wood, which is functionally inactive in the growing tree. It results from a gradual conversion of sapwood during the growth of the tree and is more rot-resisting, more resinous and impenetrable than the sapwood. The latter which forms a shell around the heartwood varies from a comparatively thin layer, as in the case of cedar or chestnut, to such a thickness that it constitutes practically the whole volume of the wood, as in the case of younger specimens of the fast-growing varieties of pines. With present methods preservatives can economically be introduced in round timbers only into the sapwood; in practically every case, there is a much higher concentration of preservative in the outer layers than in the inner layers of freshly treated sapwood (Table I).

Table I. Radial Distribution of Creosote in Typical Freshly Treated Southern Pine Poles

(Grams per 100 cc. of wood)

Sapwood Layer[a]	Specimen Number 1	2	3	4	5	6	7	Average
Outer	16.3	19.1	18.7	17.0	25.2	20.5	14.4	18.7
Intermediate	8.2	12.6	6.1	6.1	13.9	22.0	11.1	11.5
Inner	6.9	5.4	3.7	4.0	4.3	7.4	7.7	5.6

[a] Each layer 1 inch (2.54 cm.) thick.

Other forms of maldistribution of preservative are often present. For example, conditions of growth may effect an asymmetric development of the trunk of the tree. This circumferential variation in the development of the annual rings of the wood may be reflected in the distribution of preservative in the pole, so that there may be substantially more oil in one quadrant or sector than in another. Probably in most cases variations in the treatability of different sectors are caused by nonuniformity of moisture content or inherent deviations of structure. At all events the circumferential distribution is somewhat irregular in almost every observed case of pole treatment (Figure 1).

Analysis of samples indiscriminatingly taken from timbers may lead to gross errors. A true sample of a round timber must contain a volume of each annual growth ring proportional to its distance from the center of the tree and must also represent each sector of cross section of the timber. The desired result is approximated by taking increment borer cores around the circumference of the timber and bisecting each core in such a way that the segments taken for analysis approximate wedges in their significant geometrical features.

A true sample must not only represent each layer in the same proportion as it exists in the pole—that is, in a quantity directly proportional to the distance from the center—but also, at least approximately, represent each sector in the proportion that it exists in the pole. A cross-sectional slab of uniform thickness cut from approximately the mid-point of a pole closely approximates a true sample, in that it represents each concentric layer and each sector in the proper proportion. Such a sample is often too large for convenience. It may be cut into sectors by splitting repeatedly through its center. Providing these sectors, or wedge-shaped pieces, are chosen from each quadrant so that they approximately represent circumferential distribution, they may be used collectively as a sample.

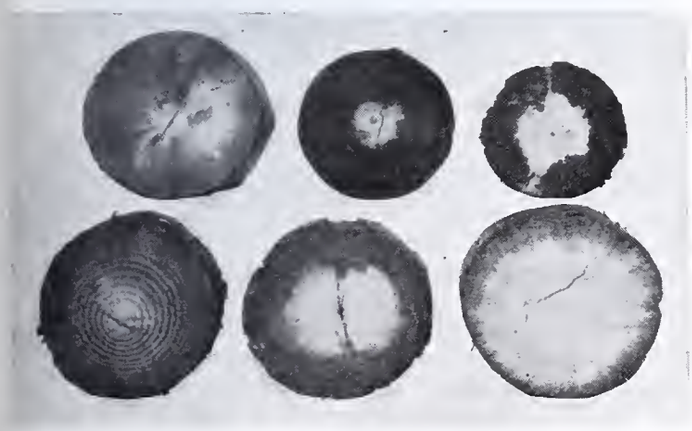

Figure 1. Distribution Patterns Encountered in Pressure Creosoted Southern Pine Poles.

This collective sample or the slab from which it is derived constitutes a satisfactorily representative sample, but such a method of sampling obviously cannot be used for repeated examinations of a pole at intervals of service or experimental exposure. In view of the idiosyncrasies of each pole, it is impossible to examine a lot of poles reliably by choice of a few poles at random. It therefore becomes essential to be able to reëxamine each pole or at least a substantial proportion of each lot of poles individually if one is to learn anything quantitative about changes of condition with time.

Corrections of Sampling Errors

The increment borer, designed for studying the growth of living trees, removes a small, solid cylindrical core which may be so taken as to extend from the surface to the center of the tree. This sample lends itself readily to the study of wood structure and penetration. Sampling a pole with this instrument (Figure 2), provided a reasonable number of borings are taken and the holes are filled with preserved wooden plugs, does not seriously injure a pole for service purposes nor greatly alter the weathering process in nearby wood. Although this sampling method has a number of advantages, it does not give a representative sample. It takes equal quantities of wood from each layer of the pole and thus incorporates in the sample too large a proportion of the inner layers.

However, if the penetration can be measured accurately and if it could be safely assumed that the concentration of the preservative is substantially constant in all portions penetrated, the results obtained from the analysis of cylindrical (increment) borings could be corrected by applying a suitable mathematical factor. This expedient has been of some value in many instances in which borings had been analyzed prior to the development of newer and more accurate methods of sampling. This correction factor may be derived as follows:

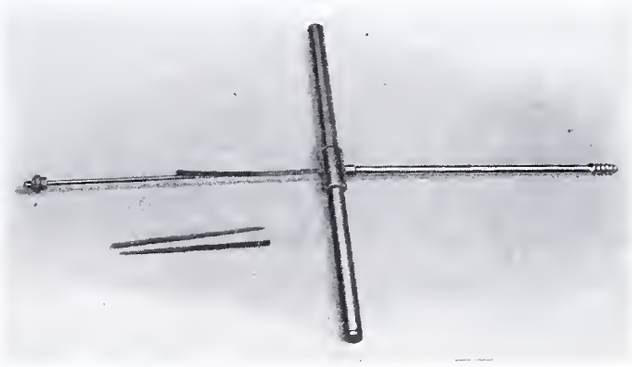

Figure 2. Increment Borer

A split boring in lower left

Assume a sector of a cylinder and a boring taken from the same pole of unit radius.

In the boring (Figure 3)

a = volume of impregnated wood
b = volume of unimpregnated wood
R = radius = 1
p = fraction of radius penetrated

The volume of the impregnated cylinder is to the volume of the entire cylinder as the altitudes of the cylinders—i. e., $\frac{a}{a+b} = \frac{p}{R} = p$ = fraction of the volume of wood which is impregnated according to the cylinder sample.

In the sector (Figure 3)

a_1 = volume of impregnated wood
b_1 = volume of unimpregnated wood

The volume of the whole sector $(a_1 + b_1)$ is proportional to R^2; that of the small sector (b_1) is proportional to the square of its radius $(R - p)^2$; that of a_1 is proportional to the difference of the squares of the two radii—i. e., to $R^2 - (R - p)^2$ or

$$\frac{a_1}{a_1 + b_1} = \frac{R^2 - (R - p)^2}{R^2} = \frac{R^2 - (R^2 - 2Rp + p^2)}{R^2} = p(2 - p) =$$

the true fraction of the pole which is impregnated as shown by the sector.

$$\frac{\text{True fraction}}{\text{Fraction shown by cylinder}} = \frac{p\,(2 - p)}{p} = 2 - p$$

$$\text{True fraction} = (2 - p) \times \text{cyclinder fraction}$$

To correct cylinder analyses merely multiply the weight of preservative found per unit volume by $2 - p$.

Accurate analyses cannot be obtained in all cases by correcting in this manner, both because of the difficulty of determining with sufficient accuracy the value of p, and because of the nonuniform distribution radially of the preservative in the impregnated portions of the pole. The error from this latter source applies to an analysis regardless of the substance in question. Preservatives in general are more or less concentrated near the surface in freshly treated poles but, depending on their solubility, volatility, and viscosity, may redistribute themselves on standing. Test posts analyzed by sampling in this fashion have shown, paradoxically, an increase in creosote oil content after one year's exposure, due to a redistribution of oil from circumference toward the center. In moisture determinations where, depending on circumstances of seasoning, almost any distribution of moisture is possible, errors of a magnitude equal to that of the true moisture content may occur. Some illustrations of the size of the errors which arise from the assumption that a cylindrical boring (without mathematical correction) is a fair sample are shown in the first column of Table II. These errors are calculated from geometrical considerations, but many of the assumptions fall within the range of actual cases. In green wood the moisture content is very much higher in the sapwood than in the heartwood, but in partially seasoned wood the moisture distribution may approach those assumed in the last two cases in the table.

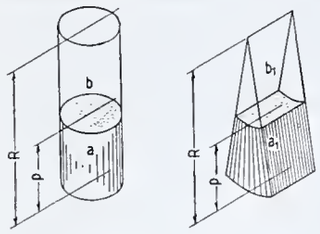

Figure 3. Comparison of Boring and Cylinder Sector

Table II. Possible Errors by Analysis of Borings from a Pole

	Penetration	Cylindrical Boring Error	Split Boring Error[a]
		%	%
Oil concentration varying linearly from maximum at surface to zero at limit of penetration	0.1 radius	− 48.3	+ 3.1
	0.2 radius	− 46.4	+ 3.5
	0.3 radius	− 44.4	+ 4.3
	0.5 radius	− 40.0	+ 5.1
	Entire radius	− 25.0	+ 3.1
	Moisture Limited to		
Moisture in inner part of pole and uniformly distributed therein	Inner 0.2 radius	+400.0	−41.5
	Inner 0.5 radius	+100.0	−15.3

[a] See later discussion.

In Table II, an assumption is made that the oil is distributed so that the concentration is a maximum at the outside and declines linearly to zero at the limit of penetration. This is the most reasonable assumption with regard to freshly treated poles and it is obvious that a mathematical correction could be applied on the basis of this assumption. However, such a correction would be somewhat complicated. Moreover, the same assumption is unjustified for old poles. In weathering there is a marked tendency for depletion to occur at the surface by evaporation, so that in extremely old poles the fairest simple assumption might be that the concentration is at a minimum at the surface and increases linearly to a maximum at the limit of penetration. Accordingly, it would be necessary to modify the basis of correction progressively with the age of the pole.

In view of these facts, a method was sought which would directly provide an approximately representative sample. A tapered twist drill was designed which would remove a sample having the mathematical properties of a wedge. This method gives an approximately true sample from symmetrical poles of any diameter by drilling just to the center of the pole and catching the shavings as they are expelled. The practical difficulties of such a method, especially loss of shavings in a breeze, make it objectionable in sampling telephone poles.

Figure 4. Diagram of a Boring Split Diagonally

A practical and approximately accurate sample is secured by taking an increment boring and discarding an appropriate part of the cylinder. For this purpose, a boring whose length is equal to the radius of the pole is sliced diagonally with a knife blade in such a way that the plane of the cut is tangential to the basal cross section of the boring at its outer end and tangential to the oppostie side of the boring at its inner end, as illustrated in Figure 4. A guillotine for doing this rapidly has been developed and is illustrated in Figure 5. The part of the boring having its small end at the center of the pole is used as the sample for analysis; the remainder is discarded. In the appendix by Peek it is shown that, if such a sample is geometrically perfect, the maximum error introduced will be 7.0 per cent provided the greater portion of the oil lies outside the half radius of the pole. In general the error will be substantially less than 7.0 per cent. By means of the equations given in the appendix, the errors resulting for the illustrative cases of Table II have been computed.

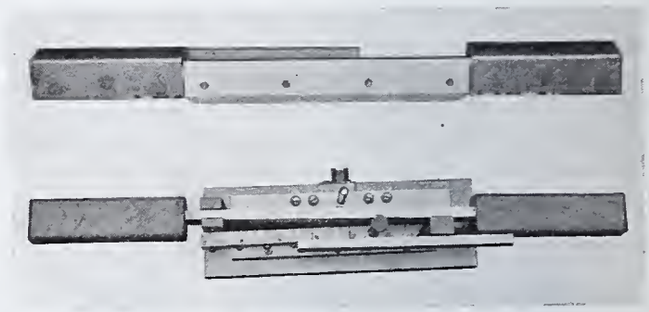

Figure 5. Boring Splitter

Top view, and above, disassembled knife

There are of course other errors which may affect such a sample. For example, the pole may be asymmetrical in structure or in penetration of preservative. To minimize this error, the pole is sampled by taking a number of borings equally spaced around its circumference and to avoid excessive weakening of the pole, somewhat distributed along its length. Each of these is diagonally split and the proper portion of each is taken to make a composite sample. There is perhaps some danger of expressing oil from the boring during the process of boring, but evidence of this has not been detected. Observation shows that the pressure is exerted outward rather than inward. There is also some error due to deviation of the dimensions of the split boring from the nominal ones on account of mechanical inaccuracy of implements. For this reason, the actual diameters of borings should be checked occasionally. Still another difficulty that is inherent in all extraction methods of analyzing for creosote oil is due to the extraction of a variable amount of resin from the wood; the weight of this resin is counted as creosote. This error is considerably lessened by discarding all the untreated portions of the borings before extracting.

Table III gives a comparison of the results obtained by the three methods of sampling. Mathematically corrected values for the cylindrical sample are included. They serve on the average to bring the results in fair agreement with the correct value, but involve an assumption as to distribution.

TABLE III. ANALYSIS OF SEVEN CREOSOTED POSTS BY THREE METHODS

(Grams per 100 cc. of total wood)

	Oil Content by Wedge Sample	P/R	$2-P$	Oil Content Cylindrical Boring	Error[a] %	Mathematically Corrected Oil Content	Error[a] %	Oil Content by Split Boring	Error[a] %
1	8.89	0.895	1.105	7.73	−13.1	8.54	− 3.96	9.73	+9.35
2	9.82	0.455	1.545	5.06	−48.3	7.84	−20.1	9.36	−4.56
3	8.57	0.573	1.427	4.80	−44.0	6.85	−20.0	9.20	+7.46
4	6.54	0.545	1.455	4.77	−26.9	6.95	+ 6.36	6.51	−0.50
5	11.00	0.494	1.506	7.42	−32.4	11.18	+ 1.75	11.81	+7.42
6	12.82	0.489	1.511	9.12	−28.9	13.77	+ 7.36	13.96	+8.85
7	10.61	0.677	1.323	7.47	−29.6	9.89	− 6.79	11.28	+6.33
Av.	9.76	...	...	6.63	−32.1	9.30	− 4.75	10.27	+5.24

[a] In all cases the wedge sample is assumed to give the true result and the "error" represents the deviation from this value. The correction involves the assumption that the concentration is uniform throughout the treated portion.

In certain cases this assumption is very faulty and the correction fails badly. The uncorrected values for the split cylinder are so near the true values that the corrections are omitted. Imperfect as they are, the uncorrected values obtained with the split boring are apparently within 10 per cent of the truth and have the great merit of involving no arbitrary assumption about the concentration gradient. They are sufficiently reproducible to afford valuable data about the progressive loss of creosote and changes in its toxicity with the lapse of years. The method is being applied both to service pole lines and experimental material in test plots. It has also been of great value in measuring uniformity and the level of quality of product from commercial treating plants.

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Appendix

R. L. PEEK, JR.

IT IS desired to compare two samples of equal length l and equal volume V, one being a wedge of height d and width at the base b, the other a cylinder of radius r bisected by a plane passing through a diagonal of a longitudinal section through the axis and perpendicular to the section.[1]

For the wedge

$$V = \frac{bdl}{2}$$

and as both samples have the same volume, and as that of the cylinder is $\frac{\pi r^2 l}{2}$, evidently

$$bd = \pi r^2$$

Area A of cross section of wedge at any point distant x from the base is given by

$$A = \frac{l - x}{l} bd = (1 - m) \pi r^2 \qquad (1)$$

where $m = \frac{x}{l}$ (fraction of length).

[1] Strictly speaking, neither the ideal (wedge) sample nor the actual (split cylinder) sample has a plane base as assumed in this formulation, as the base surface is that of the tree, which is approximately cylindrical. As in both samples the dimensions of the base are small compared with the radius of the tree, the distinction between a plane and cylindrical base has been ignored as trivial.

Typical sections of the split cylinder are shown in Figure 6. Let the perpendicular distance from the center to the boundary be ρ, as shown, positive if to the right and negative if to the left. From inspection of Figure 6

$$\rho = r - \frac{x}{l} \cdot 2r = r\left(1 - \frac{2x}{l}\right) \qquad (2)$$

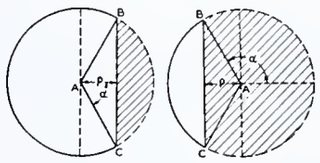

FIGURE 6. TYPICAL SECTIONS OF SPLIT CYLINDER

To obtain the area of any section there must be subtracted from the area of the circle the section cut off, shown shaded in the drawing. This shaded area is given by the area of the sector $r^2a = r^2\cos^{-1}\frac{\rho}{r}$, less the area of the triangle $A\,B\,C$, and hence

$$A' = \pi r^2 - \left(r^2 \cos^{-1}\frac{\rho}{r} - \rho\sqrt{r^2 - \rho^2}\right)$$
$$= \pi r^2 - r^2 \cos^{-1}(1 - 2m) + r^2(1 - 2m)\sqrt{1 - (1 - 2m)^2} \qquad (3)$$

Here $m = \frac{x}{l}$ as before. The ratio A'/A for any value of m is the ratio of the cross-sectional areas of the two samples (half-cylinder and wedge) at the fraction of the sample length given by m. Values of this ratio, computed by means of Equations 1 and 3, have been plotted in Figure 7 against corresponding values of m.

In the wedge sample the quantity of creosote (or other material) contained in a portion of the sample bounded by the planes $m = a$ and $m = b$ will be given by

$$Y = \int_a^b Q\,A\,l\,dm \qquad (4)$$

where A is the cross-sectional area of the sample and Q the amount of creosote or other material per unit volume at the point m. If A' is substituted for A in Equation 4, the resulting expression gives Y', the quantity of creosote lying between $m = a$ and $m = b$ in the split cylinder sample.

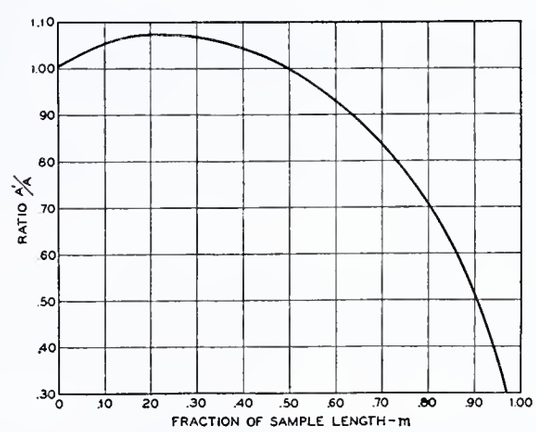

FIGURE 7. RATIO OF CROSS-SECTIONAL AREA OF SPLIT CYLINDER AND WEDGE AT SUCCESSIVE DEPTHS

The two samples have, as shown by Figure 7, the same cross-sectional area at $m = 0.5$. For values of m between 0.0 and 0.5, the ratio A'/A varies from 1.0 to a maximum of 1.07 and then back to unity. For values of m greater than 0.5, A' is always less than A. From this it at once follows that if, as is in general the case, the greater portion of the creosote is in the outer portion of the pole (between the cylinders $m = 0$ and $m = 0.5$), Y' will be greater than Y—i. e., the value for the creosote content obtained from the split cylinder sample will be greater than the correct value as given by the wedge sample. It is also evident that the greatest possible error in this case will be that corresponding to the maximum ratio of A'/A (1.07), or 7 per cent, and that the error will in general be less than this.

To determine the error for any given distribution of creosote or moisture it is necessary to integrate Equation 4 with Q given the values as a function of m that express this distribution. As any curve can be approximated by a series of straight lines, approximations to any concentration gradient $[Q = f(M)]$ can be made by a series of straight lines, and therefore it will be sufficient to integrate Equation 4 for the case

$$Q = cm + k \tag{5}$$

Substituting in Equation 4 the value of Q given by Equation 5 and the value of A given by Equation 1, integration yields

$$Y = \pi r^2 l \Big|_a^b \left[\frac{cm^2}{2} - \frac{cm^3}{3} + km - \frac{km^2}{2}\right] \tag{6}$$

the value of Y for the wedge.

For the split cylinder the same procedure may be followed, taking the value of $A(A')$ given by Equation 3, and there is obtained

$$Y' = r^2 lc \Big|_a^b \left[\frac{\pi m^2}{2} - \left(\frac{1}{16}[2(1-2m)^2 - 1] - \frac{1}{4}(1-2m)\right)\cos^{-1}(1-2m) + \left(\frac{3}{32}(1-2m) - \frac{1}{4} + \frac{m}{6}(1-(1-2m)^2) + \frac{1}{48}(1-2m)[1-(1-2m)^2]\right)\sqrt{1-(1-2m)^2} + \frac{1}{32}\sin^{-1}(1-2m)\right] + r^2 lk \Big|_a^b \left[\pi m + \frac{1}{2}(1-2m)\cos^{-1}(1-2m) - \frac{1}{2}\sqrt{1-(1-2m)^2} + \frac{1}{6}\left(1-(1-2m)^2\right)^{\frac{3}{2}}\right] \tag{7}$$

Having found Y and Y' by means of Equations 6 and 7 for any given distribution, the error caused by using the split cylinder is given (in per cent of the true value) by the expression $100\,\frac{Y' - Y}{Y}$. Similarly, the apparent creosote content obtained from a split cylinder sample may be corrected by multiplying by the ratio $\frac{Y}{Y'}$, if Y and Y' are evaluated for some assumed distribution, such as that in which the concentration is constant from $m = 0$ to $m = p$, and zero for $m > p$.

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Occlusion of Water by Potassium and Sodium Chlorides

The Influence on Indirect Determination of Sodium

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THE mixed salts of potassium and sodium in the form of their chlorides are often weighed after ignition at approximately 500° C. in preparation for the determination of sodium by difference after the determination of potassium. Ignition to the fusion temperature is not advisable, since these salts are appreciably volatile at their melting point Heating to 500° C. is usual, since it is recognized that prohibitive amounts of water are occluded at lower temperatures.

The present investigation was carried out to establish the amount of occluded moisture in potassium and sodium chlorides when these have been prepared by various methods and dried or ignited at various temperatures up to and beyond the melting point. The results obtained have a direct bearing upon the accuracy with which sodium can be determined in the presence of potassium when starting with weighed mixtures of these chlorides and determining the sodium by difference.

Preparation of Materials

Chemically pure potassium and sodium chlorides were dissolved in water and the solutions crystallized by the following procedures:

1. Slow evaporation on the hot plate followed by centrifugalizing and drying at 140° C. Samples 1 and 2.
2. Precipitation of the saturated solution using a stream of gaseous hydrochloric acid. Crystals centrifugalized and dried at 140° C. Samples 3 and 4.
3. Per-crystallization[1] using collodion sack as semi-permeable membrane. The crystals thus obtained were dried at 140° C. These crystals were in the form of needles and were of low bulk density. Samples 5 and 6.

The odd-numbered samples were sodium chloride and the even numbers potassium chloride.

Apparatus and Method of Testing

Small samples of the salts prepared by the three methods described were weighed into covered crucibles and dried for 1 hour at the temperatures noted below the fusion point in an electrically heated crucible furnace, cooled, and weighed. The loss in weight determined the moisture liberated at the temperature employed. Loss by decrepitation was prevented by a crucible cover. A J. Lawrence Smith crucible was generally employed and the samples were placed in the bottom half. The top half and the cover were shielded by a piece of transite board drilled to receive the crucible and allow the upper third and cover to project above. The crucible cover was kept cool by a porcelain crucible filled with water which was replaced as it boiled away. Temperatures were measured by a platinum–platinum rhodium thermocouple and potentiometer or by a quartz, nitrogen-filled mercury thermometer. The time of heating for determinations above the melting point was 20 minutes only.

Table I. Dehydration of Potassium and Sodium Chlorides at 550° and 900° C.

Sample	Sample Weight Range	Loss at 550° C.[a]		Loss at 900° C.[a]		Total Loss	Ratio of Loss 550°/900°
	Grams	*Mg.*	%	*Mg.*	%	%	
NaCl 1	0.7555–0.9770	1.75	0.196	0.62	0.069	0.264	2.9/1
NaCl 3	0.6822–0.9978	2.18	0.248	0.97	0.110	0.358	2.25/1
NaCl 5	0.8783–1.1560	3.85	0.393	0.79	0.081	0.475	4.9/1
KCl 2	0.7096–1.2272	1.53	0.156	0.63	0.064	0.217	2.4/1
KCl 4	0.8350–1.3131	4.84	0.487	0.78	0.079	0.566	6.2/1
KCl 6	0.6493–1.1812	1.69	0.200	0.58	0.069	0.269	2.9/1

[a] Average of six determinations.

The total occlusion of water by sodium chloride increases when precipitated from hydrochloric acid as compared to crystallization from water. This result would not be predicted, since in the hydrochloric acid precipitation the crystals are very finely divided as compared to those obtained from evaporation of an aqueous sodium chloride solution. The total occluded water in per-crystallized sodium chloride is roughly twice that found in crystals obtained from aqueous solutions. The ratio of water liberated at 550° C. as compared to the water liberated at 900° C. follows closely values which would be predicted by comparison of crystal magnitudes. The ratio increases as the particles diminish in size.

The same relationships are found using potassium chloride, except that occlusion of water in the per-crystallization process is roughly half as great as that for sodium chloride similarly prepared. The ratio of water liberated at 550° compared to that at 900° C. is correspondingly low.

From an analytical point of view it may be said that mixed crystals of sodium and potassium chlorides occlude too much water after drying at 550° C. to be negligible and weighing after fusion with precautions to prevent volatilization, which at 900° C. would be prohibitive, is recommended. The residual moisture after drying at 550° C. averages 0.08 per cent in the three types of crystallization employed.

[1] Kober, P. A., *J. Am. Chem. Soc.*, **39**, 944 (1917).

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Determination of Nitrates

Modification of the Devarda Method

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THE Devarda method for the determination of nitrates is coming more and more into use for the determination of nitrates in fertilizer mixtures (*1*) and in plant materials (*2*). The reduction is accomplished in a sodium hydroxide solution and in the case of inorganic salt mixtures the distillation is generally carried out in large Kjeldahl flasks with a Davisson (*3*) scrubber with precautions to minimize frothing.

Magnesium oxide is used for the determination of ammonia in both organic and inorganic materials, primarily because of its slight effect, if any, upon nitrogenous organic materials. The object of the present investigation was to determine whether magnesium oxide could be used instead of sodium hydroxide in the Devarda method for the determination of nitrates. Such a modification would offer many advantages.

Experimental

The first step was to try the modification on solutions of known concentrations. Solutions of sodium nitrate and of ammonium chloride (0.02 *N*) were made from c. p. chemicals and analyzed—the ammonium chloride solution for ammonia by distillation with magnesium oxide and the sodium nitrate solution for nitrates by the official Devarda method. The results, given in Table I, are averages of triplicate determinations. In view of the small weights of nitrogen used, the variations between the quantities used and those found were considered as being within the limits of experimental error. The percentages of recovery given in Tables II and III were therefore based on the theoretical values of the solutions used.

Table I. Analysis of 0.02 *N* Solutions of Ammonium Chloride and Sodium Nitrate

Chemical	Solution	Nitrogen Found	Nitrogen Theoretical	Percentage Recovery
	Cc.	*Mg.*	*Mg.*	
Ammonium chloride	15	4.31	4.20	102.6
Ammonium chloride	20	5.71	5.60	102.0
Sodium nitrate	15	4.31	4.20	102.6
Sodium nitrate	20	5.74	5.60	102.5

The distillation in the modified procedure was carried out in small Kjeldahl flasks (500 cc.) and without scrubbing bulbs for 1.5 hours, as in the standard Devarda method using 2 grams of magnesium oxide and 3 grams of Devarda alloy. The boiling proceeded quietly without foaming or frothing and required no precautions. It was difficult to account for the low recovery indicated by Table II, in view of the fact that the nitrate was being reduced with magnesium oxide, as registered by the 61 to 88 per cent recoveries obtained.

Table II. Nitrogen Recovered from Sodium Nitrate
(Distillation for 90 minutes specified by official Devarda method)

Sodium Nitrate Concentration		Nitrogen Found	Nitrogen Theoretical	Percentage Recovery
	Cc.	*Mg.*	*Mg.*	
0.02 *N*	15	3.7	4.2	88.1
0.02 *N*	20	4.8	5.6	85.7
0.1 *N*	15	13.0	21.0	61.9
0.1 *N*	20	19.8	28.0	70.7

After a study of several factors, such as quantities of the Devarda alloy and of magnesium oxide, rate of boiling, and volume of distillate, it was found that the proposed modification required distillation for about 2.5 hours instead of the usual 1.5 hours. When 300 cc. of water were added to the Kjeldahl flasks and the boiling was regulated to require 2.5 hours, the results obtained were close to theoretical.

The modified method permits determination of ammoniacal and nitrate nitrogen in the same solution. A mixed solution containing equivalent quantities of ammonium chloride and sodium nitrate was first distilled with magnesium oxide and the ammonia determined. Enough water to give a total volume of 300 cc. and 3 grams of Devarda alloy were then added to the residues in the Kjeldahl flasks and the nitrate nitrogen was determined, with the results given in Table III.

Table III. Ammoniacal and Nitrate Nitrogen in a Single Aliquot
(Modified Devarda method)

Ammonium Chloride and Sodium Nitrate			Theoretical Nitrogen in Each Form	Ammonia Nitrogen Found		Nitrate Nitrogen Found	
Portion	Concentration of each	Taken					
		Cc.	*Mg.*	*Mg.*	%	*Mg.*	%
1	0.02 *N*	15	4.20	4.21	100.2	4.28	101.9
2	0.02 *N*	20	5.60	5.66	101.0	5.71	101.9
3	0.1 *N*	10	14.0	14.06	100.4	13.99	100.0

The standard and modified procedures were then tried on a commercial fertilizer mixture, A, and on fertilizer B, obtained from the Soil Fertility Laboratory, Department of Agriculture. As fertilizer A contained organic matter, large Kjeldahl flasks were used as in the official procedure. The results, given in Table IV, are averages of three determinations except when specified.

The advantages of the modified procedure were marked in the case of the fertilizers, especially fertilizer A, which contained organic matter and foamed badly in the official procedure.

Table IV. Ammoniacal and Nitrate Nitrogen in Complete Fertilizers
(Modified and official Devarda methods)

Fertilizer	Total Nitrogen	Ammoniacal and Nitrate Nitrogen: Standard Devarda	Ammoniacal and Nitrate Nitrogen: Modified Devarda	Modified Devarda: Ammoniacal nitrogen	Modified Devarda: Nitrate nitrogen	Modified Devarda: Ammoniacal and nitrate nitrogen (calc.)
	%	%	%	%	%	%
A	3.44	2.55	2.48	2.29	0.26	2.55
B	3.72[a]	3.76	3.64[b]	1.64	2.09[c]	3.73

[a] Average of 4 determinations.
[b] Average of 5 determinations.
[c] Average of 6 determinations.

It was found that the sulfates of magnesium, copper, zinc, and aluminum interfered with the recovery of nitrate nitrogen by the proposed modification. The interference varied with the quantity of the sulfates present and with the size of the particles of the Devarda alloy. For example, 1 gram of magnesium sulfate caused interference when 3 grams of 20-mesh Devarda alloy and 2 grams of magnesium oxide were used. On the other hand, 0.3 gram of magnesium sulfate caused no interference under the same conditions, but interference developed when a coarser Devarda alloy was used. When 1 gram of the chloride of any of the above elements was present, no interference was noted when 20-mesh Devarda alloy was used. Interference did occur when coarser alloy was used.

The interference of the sulfates and chlorides of magnesium, copper, zinc, and aluminum is probably due to the lowering of the active alkalinity of the saturated magnesium hydroxide solution. The pH value of a saturated solution of magnesium hydroxide is relatively low—about 9.8—and anything that tends to lower it still further would probably reduce the

alkalinity of the solution below the minimum required for the proper functioning of the Devarda alloy.

The use of barium chloride to overcome the interference of the above-mentioned sulfates was not entirely successful. Nevertheless, it was found that a 1-gram addition of barium chloride materially shortened the distillation period required by the modified method for the complete recovery of nitrate nitrogen from solutions that contained no interfering substances. When barium chloride was added, distillation for 1.5 to 2 hours was sufficient for complete recovery of the nitrate nitrogen. It has not been determined whether this time-shortening effect was due to the rise in boiling point or to some other cause. The same effect can be obtained by the use of 5 instead of 2 grams of magnesium oxide but, if the determination of organic nitrogen in the residue from the ammoniacal and nitrate nitrogen determinations is desired, the use of 1 gram of barium chloride rather than the additional 3 grams of magnesium oxide would be more convenient.

The interference of the sulfates is not considered a serious drawback in the use of the proposed modification, as these are seldom found in nitrate-containing materials, in proportions large enough to cause interference. It has been determined, however, that a 5-gram charge of the 20-mesh or a 3-gram charge of a 40-mesh Devarda alloy overcomes completely the interference caused by quantities of as much as 1 gram of the sulfates mentioned.

It was found advisable, with both the official and the modified Devarda methods, to test the residue for nitrates in case of doubt as to complete recovery of the nitrate nitrogen.

The modified method is also being adapted for the determination of nitrates in plant materials.

Procedure

The modified procedure is as follows:

Introduce a charge of mixed salt, equivalent to not more than 0.1 gram of nitrogen, into a 500-cc. Kjeldahl flask; add 200 cc. of water and 5 grams of magnesium oxide. Collect about 100 cc. of distillate in a measured quantity of standard acid for the determination of ammoniacal nitrogen. Then disconnect the Kjeldahl flask and add 200 cc. of distilled water; add 3 grams of 20-mesh Devarda alloy and distill for 1.5 to 2 hours into a measured quantity of standard acid for the determination of nitrate nitrogen. If the sulfates of magnesium, copper, zinc, or aluminum are present in quantities above 0.3 gram, use 5 instead of 3 grams of Devarda alloy.

If no ammoniacal salts are present, add the magnesium oxide and Devarda alloy simultaneously and proceed as above.

Summary

Magnesium oxide was substituted for sodium hydroxide in the Devarda method.

The modified method admits determination of ammonia and of nitrate nitrogen in the same solution, prevents frothing, and obviates precautions against passage of spray into the standard acid.

The distillation period stipulated is longer than that required by the official method. Addition of either barium chloride or larger quantities of magnesium oxide shortened the distillation period required for complete recovery of the nitrate nitrogen.

When present in relatively large quantities, the sulfates and, in a lesser degree, the chlorides of magnesium, zinc, copper, and aluminum interfered with the complete recovery of nitrate nitrogen by the modified procedure when coarse Devarda alloy was used. This difficulty was overcome by using more finely divided Devarda alloy or by increasing the commonly used quantities of the 20-mesh Devarda alloy.

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Rapid Potentiometric Method for Quantitative Determination of Copper in Alloys

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The industrial importance of copper has led to the investigation of many methods of determination, of which the electrolytic is the most accurate. However, the time required, the technic, and the use of considerable platinum have made desirable a more rapid and easy method of analysis. The large potential break shown in the titration curve of potassium thiocyanate with potassium iodate using a bimetallic electrode system, as noted by Fenwick (*2*), has led to the suggestion by Kolthoff (*5*) that a similar break might occur with a monometallic system. The method herein described involves the precipitation of copper as cuprous thiocyanate, with an excess of standard thiocyanate solution, filtering off the precipitate formed, and titrating potentiometrically the excess thiocyanate with potassium iodate.

Among the methods for the determination of copper as cuprous thiocyanate, the following three are now in general use: (1) igniting to the oxide and weighing; (2) titrating with potassium permanganate; (3) adding an excess of potassium iodate and potassium iodide and titrating the liberated iodine with sodium thiosulfate. A less frequently used method is that of Jamieson, Levy, and Wells (*4*), involving the direct titration of copper as cuprous thiocyanate, using chloroform. The present method avoids the large ignition errors of the first, the necessity of empirical factors of the second, and the tedious chloroform titration of the last. Another factor in its favor is the short time required for analysis, a complete determination requiring about 30 minutes.

Discussion

According to Kolthoff (*5*), the reaction involved in the titration of the thiocyanate ion with the iodate ion is:

$$4CNS^- + 6IO_3^- + 6Cl^- + 8H^+ = 4SO_4^= + 6ICl + 4HCN + 2H_2O$$

Experience has shown, however, that the thiocyanate must be standardized against the iodate and also against pure copper, whereby the method is rendered quantitative. The amount of hydrogen cyanide generated during the reaction is almost unnoticeable.

The platinum electrode used in this investigation was a

small coiled wire type, and was balanced against a saturated calomel electrode. The stirrer and electrode set-up of the Kelly electrometric titration apparatus was found to be the most convenient for the titration. A Leeds & Northrup Type K potentiometer was employed.

The authors have found that for a concentration of hydrochloric acid of less than 25 per cent an incomplete reaction results, possibly due to the hydrolysis of iodine monochloride. The best results were obtained with an acid concentration of 40 to 50 per cent when the break is very sharply defined, and the color change warning of the end point is excellent.

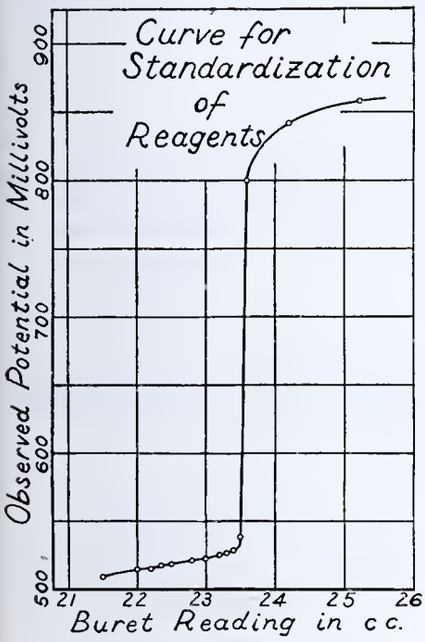

Figure 1

After frequent use, the electrode loses its sensitivity. Biilmann's (*1*) suggestion that the electrode be heated to white heat in an alcohol flame is satisfactory.

The cuprous thiocyanate precipitate becomes granular upon boiling. However, since the solubility of the precipitate in hot water is appreciable, it is necessary to cool the liquid before filtration. Since the cuprous thiocyanate is not completely insoluble in cold water, it was found desirable to use the same quantity of wash water in both standardization and determinations, limiting the quantity to about 40 cc.

In the method to be described, the potential break is very sharp, and shows a rise of from 200 to 350 millivolts upon the addition of one drop of potassium iodate at the end point. There is ample warning of the approach of the end point, due to a definite color change in the solution, the change being nearly though not altogether sharp enough to enable visual titration.

In determining the inflection point of the titration curve the method given by Hostetter and Roberts (*3*) has been found both simple and reliable, although the break in the curve is so sharp that for routine work no special method is required to find the end point. The plotting of a curve is therefore not essential. Two typical titration curves are shown in Figures 1 and 2.

In general, any substance which precipitates as a thiocyanate will interfere. The most commonly encountered of these is lead, and it should be removed as the sulfate. Tin should be filtered off as metastannic acid. Nickel, zinc, and small quantities of iron do not interfere with the titration, thus making the method especially applicable to the analysis of German silver.

Procedure

Dissolve the sample, containing 0.1 to 0.2 gram of copper, in 3 to 4 cc. of nitric acid (sp. gr. 1.42) contained in a 150-cc. Erlenmeyer flask. Heat gently until there are no more brown fumes evolved. Add 3 cc. of concentrated sulfuric acid (sp. gr. 1.84), and heat until about 3 minutes after the first appearance of the dense sulfur trioxide fumes, keeping the flask in constant motion during this process. Cool and dilute with water to about 15 cc., carefully neutralize with concentrated ammonium hydroxide until the appearance of a deep blue color, then pour in 10 cc. of a saturated solution of sulfurous acid. Add from a buret a measured volume of standard potassium thiocyanate solution, making sure that an excess is present. Heat the solution containing the flocculent white precipitate over a free flame, with constant rotation of the flask, until there can be detected no more evolution of sulfur dioxide. Where the sample is such that the amount of copper exceeds 0.1 gram, care should be taken in boiling off the excess sulfurous acid, since the large amount of precipitate has a tendency to cause bumping. This is easily avoided, however, by swirling the precipitate about in the flask during heating. The heating causes the precipitate to become granular. Cool to room temperature, and filter through a Gooch crucible with an asbestos pad of medium thickness. Wash with two 20-cc. portions of cold water.

Transfer the filtrate to a beaker suitable for titration, and rinse the filter flask with two 50-cc. portions of hydrochloric acid (sp. gr. 1.19), which must be added to the solution in the beaker. Dilute with water to a volume of 250 cc. Titrate potentiometrically with potassium iodate, which has been standardized against the potassium thiocyanate used. The addition of potassium iodate may be quite rapid until the yellow-brown color, which appears at first, begins to assume a green tone. Then titrate drop by drop until the point of maximum inflection, which is the end point. In the titration set-up, the platinum electrode is positive. If a curve of potential readings is to be plotted, it is essential that the readings of the potentiometer be obtained directly after the addition of each portion of the potassium iodate, otherwise polarization results. The stirrer used with the apparatus should be kept in constant motion during the titration, especially when potentiometric adjustments are being made.

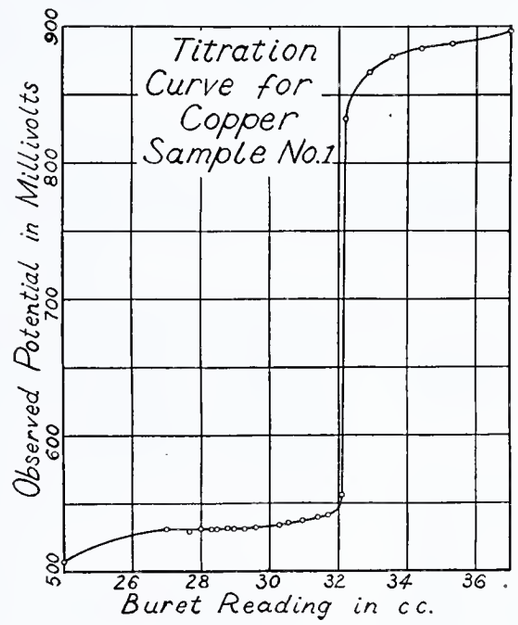

Figure 2

In their work the authors have found the use of 0.02 *M* potassium iodate and 0.05 *M* potassium thiocyanate to give a very satisfactory ratio. It is not necessary to weigh either of these reagents accurately, as they are standardized by titration.

Table I. Standardization of Potassium Iodate against Thiocyanate

Potassium Thiocyanate	Potassium Iodate	Ratio	Rise in Potential
Cc.	*Cc.*		*Mv.*
5.00	20.05	4.010	260
5.00	20.05	4.010	259
5.03	20.15	4.006	278

Standardization of Potassium Iodate. The potassium iodate to be standardized is titrated against a 5-cc. portion of the potassium thiocyanate, first adding 50 cc. of concentrated hydrochloric acid, and diluting to 100 cc. The end point is obtained exactly as in the case of the actual copper deter-

Table II. Titration of Copper Samples

Weight of Sample	Copper Present		Total KCNS Used	KIO_3 Used	KIO_3/KCNS	KCNS/Cu	Copper Found	Error		Rise
Gram	%	*Gram*	*Cc.*	*Cc.*	*Cc.*		*Gram*	*Gram*	%	*Mv.*
0.1064	...	0.1064[a]	32.00	13.18	3.800	0.003745	0.1068	+0.0004	+0.37	276
0.1078	64.96[b]	0.07003	23.60	18.77	3.800	0.003745	0.06988	−0.00015	−0.21	208
0.1472	60.57[b]	0.08916	27.00	12.36	3.800	0.003745	0.08894	−0.00022	−0.24	303
0.1105	...	0.1105[a]	32.00	11.95	4.010	0.003823	0.1109	+0.0004	+0.36	274
0.0999	...	0.0999[a]	30.00	15.40	4.010	0.003823	0.1000	+0.0001	+0.10	310
0.1059	64.96[b]	0.06879	20.10	8.37	4.010	0.003823	0.06885	+0.00006	+0.09	300
0.1274	64.96[b]	0.08276	26.10	17.88	4.010	0.003823	0.08273	−0.00003	−0.04	202
0.2248	60.57[b]	0.13616	38.36	15.37	4.010	0.003939	0.13601	−0.00015	−0.11	267
0.2150	60.57[b]	0.13023	37.17	16.54	4.010	0.003939	0.13019	−0.00004	−0.03	247
0.2814	60.57[b]	0.17044	47.20	15.55	4.010	0.003939	0.17064	+0.00020	+0.11	355

[a] Nichols Copper Co., special sample (99.993 per cent copper).
[b] V. L. Logo, analyst, Fales Chemical Co.

mination. The titer obtained gives the potassium iodate–potassium thiocyanate ratio. Table I shows typical results for a standardization.

Standardization of Potassium Thiocyanate. The potassium thiocyanate need not be accurately weighed, but must be standardized by titration against a sample of known copper content, or against a sample of pure copper. For this standardization, the method should be carried out exactly as described above, and a titer obtained of grams of copper per cubic centimeter of potassium thiocyanate.

Analytical Results. A number of samples of pure copper and German silver were analyzed by this method. Typical results are given in Table II.

Summary

A rapid potentiometric method for the determination of copper in certain alloys has been investigated and been found particularly suitable for German silver analysis, but is also applicable to the analysis of other alloys if interfering elements are first removed. The effects of acid concentrations have been investigated. Pretreatment of the platinum electrodes may be necessary. It is not required that a titration curve be plotted, thus reducing the time of a complete analysis to approximately 30 minutes.

Acknowledgment

The authors wish to thank H. A. Fales and J. J. Beaver of Columbia University for helpful criticism of the manuscript.

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Combustion Method for the Determination of Iodine in Plant Material

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Reliable information concerning the iodine content of forage crops and foods is important from the standpoint of nutrition and good health.

Iodine usually occurs in minute quantities in plant material grown under normal conditions in a fertile soil, and has an extremely important function in the metabolism of animals. The Kentucky Agricultural Experiment Station is now investigating the iodine content of forage crops and foods produced in the principal soil areas of the state. The authors have previously reported on the iodine content of soil and waters in Kentucky (*5, 6*). New methods for the determination of iodine in various kinds of organic matter by combustion with pure oxygen gas in closed systems have been published in recent years (*1–4*). A study of these methods reveals some points to be desired in the way of less complicated apparatus and technic. The attainment most desired is complete combustion of rather large samples of plant material at a uniform rate and at a moderate temperature, together with as complete recovery of iodine as is possible. After a considerable number of check determinations (duplicate determinations being made on all samples) with the apparatus described in this paper, the authors feel that substantial progress has been attained in devising a method whereby considerable quantities of plant material can be completely burned in a closed system, without the customary white fumes mentioned by previous authors, and iodine and other elements which occur in small amounts determined quantitatively.

The set-up of the apparatus as used in the authors' laboratory is shown in Figure 1.

Procedure

A sample of 50 grams of finely ground, air-dry, plant material is weighed, transferred into a porcelain dish, and thoroughly mixed with 10 grams of finely pulverized calcium oxide and 10 grams of finely pulverized copper oxide. The sample is then distributed in 3 alundum boats which are put end to end, in the large combustion tube. The right end of the large combustion tube is closed tight with a rubber stopper which carries a glass tube connecting with the wash bottle. The wash bottle on the left is connected to a suction pump. The current is connected to the electric furnace and when tube 3 attains a red heat air is drawn through the system and the first burner on the left of the gas furnace is lighted. After a short time the heat from this burner sets the plant material in the first boat on fire and a moderately rapid current of air drawn through the tubes and the turning on of other burners of the gas furnace at the proper time keeps the sample burning at a slow and uniform rate, somewhat in the manner of a lighted cigar. Any unburned vapors from the sample are drawn over the red-hot platinized asbestos catalyst where they are completely burned and the iodine vapors are carried into the gas wash bottles and absorbed.

After the combustion of the sample is completed the sources of heat are turned off and the apparatus is cooled by continuing to draw the current of air through the system. The suction pump is turned off, the boats are carefully removed, and the ash is digested and leached with hot distilled water. The filtrate

from the ash is combined with the potassium carbonate solutions from the absorption flasks and evaporated to dryness. (The authors have tried a solution of sodium bisulfite as suggested by McClendon but were unable to recover the iodine quantitatively. Accordingly a solution of potassium carbonate has been used in these experiments.) Just enough distilled water is added to dissolve the residue and the solution is transferred to a separatory funnel of the proper size. Enough 95 per cent ethyl alcohol is added to form two immiscible layers and the funnel is shaken vigorously for about 10 minutes. The aqueous portion of the solution is run into another separatory funnel and the process of extraction repeated three times. The alcoholic extracts which contain the iodine are combined and evaporated slowly to dryness so as to avoid spattering caused by too rapid boiling of the alcohol.

The residue is dissolved in a few drops of water, filtered into a small separatory funnel, and made slightly acid with sulfuric acid. About 3 cc. of a saturated solution of sulfurous acid are added, and the funnel is stoppered and vigorously shaken for about 1 minute to reduce iodate to iodide, after which 1 ml. of carbon disulfide, accurately measured, and about 2 ml. of a 10 per cent solution of sodium nitrite are added. The funnel is stoppered and vigorously shaken for about 1 minute and the carbon disulfide allowed to settle. If it has a slight pink color, all the iodine has been absorbed. However, if the carbon disulfide has a deep pink color, it is run into a centrifuge tube, 1 ml. of carbon disulfide added, and the extraction repeated until the last portion has only a faint color. The extracts are combined and centrifugalized, and a portion is compared in a microcolorimeter with an iodine standard prepared in a similar way. The results are reported in parts per million if high, or parts per billion if low.

Table I. Experiments to Test Method

Plant Material Used	Amount (Air-Dry)	Iodine Added	Catalyst Used	Iodine Recovered Fusion	Iodine Recovered Combustion in quartz tubes
	Grams	*Gram*	*Grams*	*Gram*	*Gram*
Sawdust (pine)	25	0.0000	None	0.0000	Trace
	25	0.000764	None	0.000760	...
	25	0.00190	10 (CaO) 10 (CuO)	...	0.001847
			$Ni(NO_3)_2$	*P. p. b.*	*P. p. b.*
Persimmon leaves	50	.....	3	160	180
	50	.....	3	175	183
Forest leaves	50	.....	3	127	120
	50	.....	3	147	133
Pine needles	50	.....	3	476	470
	50	.....	3	510	470
Beet tops	50	.....	3	540	590
Lespedeza	50	.....	3	535	600
	50	.....	3	521	600
Tobacco (dark)	50	.....	3	1400	1520
Tobacco, Burley	50	.....	3	1600	1680
Hay, soy bean, C-608a	50	.....	3	...	80
Hay, timothy, No. 97955	50	.....	3	...	600
Hay, red clover, No. 97972	50	.....	3	...	500
Hay, orchard grass	50	.....	3	...	1,200
Hay, bluegrass, No. 99494	50	.....	3	...	588
Mixed grain ration (corn, wheat, oats, linseed oil meal, alfalfa leaf meal)	50	.....	3	...	356
Hay, soy bean, C-1172, 1933 crop	50	.....	5	...	390
	50	.....	8 [$Ce(NO_3)_4$]	...	395
	50	.....	20 (CuO)	...	420
	50	.....	10 (CuO) 10 (CaO)	...	388
Hay, (mixed) timothy, red clover, crabgrass, 2nd cutting, 1933	50	.....	10 (CaO) 10 (CuO)	...	324
Corn, grain, yellow, C-1064, 1933	50	.....	5 [$Ni(NO_3)_2$]	...	77
	50	.....	10 (CaO) 20 (CuO)	...	90
Broom sedge	50	.....	[$Ni(NO_3)_2$]	...	85
	50	.....	10 (CuO)	...	104

A number of duplicate determinations were made on several different plant materials, using different catalysts alone and in combination. The results obtained are contained in Table I.

Discussion of Results

From Table I it is apparent that fairly consistent results for iodine in several different kinds of plant material can be obtained with the combustion apparatus described. The principal advantages of the apparatus are moderate cost, simplicity, stability, and provision of a means, with the use of the proper kind and amount of catalysts, for the complete combustion of plant material without smoke or other visible vapors passing out through the exit end of the system, in about one-fourth of the time required for an iodine determination by fusion with potassium hydroxide.

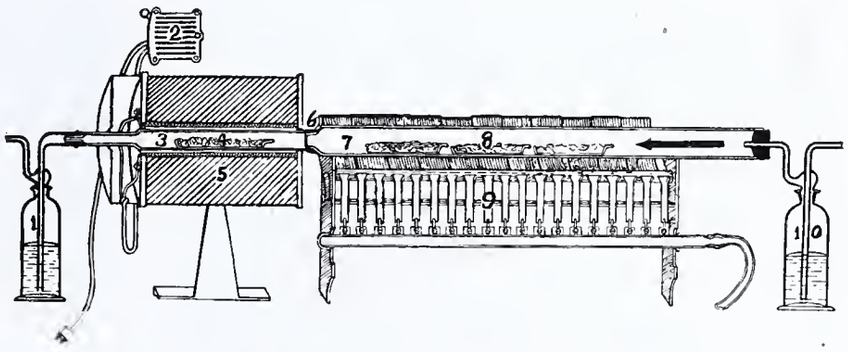

Figure 1. Diagram of Apparatus

1. Absorption bottle containing 5 per cent potassium carbonate (2 bottles used)
2. Rheostat
3. Silica catalyst tube
4. Platinized asbestos catalyst
5. Electric tube furnace, maximum temperature 1100° C.
6. Asbestos cement seal, sealing large combustion tube to smaller tube containing catalyst
7. Silica combustion tube
8. Alundum boats containing sample
9. Gas combustion furnace
10. Wash bottle containing 10 per cent potassium hydroxide

Several different catalytic agents which give up oxygen during the combustion have been tried and found satisfactory. When the finely ground plant material is wet with a 10 per cent solution of nickel nitrate and dried at 100° C., very satisfactory combustion is obtained. However, a mixture of powdered lime and finely pulverized copper oxide is as effective and more easily prepared and mixed with the plant material than the nickel nitrate. The copper oxide dust adheres and forms a film around the particles of plant material and furnishes oxygen for the combustion. The lime absorbs carbon dioxide to form calcium carbonate and apparently assists in the combustion without furnishing any oxygen.

Some samples of plant material were found to contain considerably more iodine than others, indicating either that different species of plants vary in their capacity to absorb iodine or that the soil in which they grew contained different amounts of this element.

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Estimation of Phytin Phosphorus

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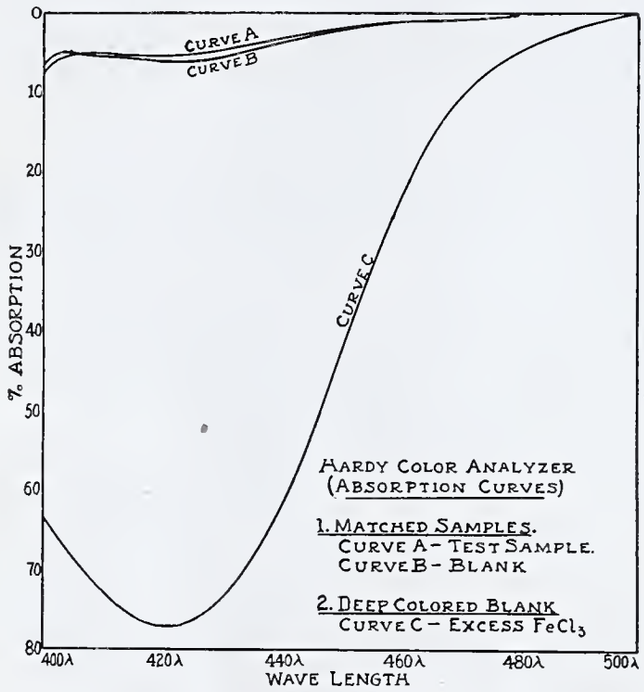
THE nutritional value of phosphorus varies with the type of compound to which it is bound. Because of these differences, in working with plant materials, especially grains, an accurate method is needed for the determination of the peculiar type of phosphorus which prevails to the extent of 70 to 90 per cent in grains and seeds.

In nature this so-called phytin phosphorus presumably occurs as sodium and magnesium salt of inositol hexaphosphoric acid, though Posternak (*6*) has suggested that the sodium-calcium salt occurs in nature, with the formula $C_6H_6O_{24}P_6Ca_2Na_8 \cdot 3H_2O$. Both Anderson (*1*) and Posternak have prepared phytic acid, $C_6H_{18}O_{24}P_6$, from various plant materials. It seems likely, therefore, that phytin phosphorus occurs as some salt of inositol hexaphosphoric acid (phytic acid).



The best method which has been offered is that of Heubner and Stadler (*4*). Phytin phosphorus is extracted from pulverized plant material with 2 per cent hydrochloric acid for 3 hours, filtered by gravity through hardened filter paper, and precipitated from the filtrate with ferric chloride in acid solution with the formation of insoluble ferric phytate. Ammonium thiocyanate is used as indicator of the ferric thiocyanate which forms after all of the ferric phytate has been precipitated.

This method has been modified several times. Rather (*7*) has used a 1.2 per cent acid solution for the extraction of the grain. Averill and King (*3*) have used a strong ferric chloride solution (the upper limit suggested by Heubner) for titration. Knowles and Watkin (*5*) have used sodium salicylate rather than ammonium thiocyanate as indicator, on the basis that the pink end point is easier to read than the yellow-brown end point given by the ammonium thiocyanate. In the authors' hands these modifications have been inconsequential and have not removed the chief difficulty of the Heubner determination: titration of a solution containing a slow-settling colloidal precipitate. Check titrations are extremely difficult because the end point is uncertain.

The authors have tested the suggestion of Andrews and Bailey (*2*) that this difficulty can be removed by titrating the unknown short of the end point and then completing the titration on the filtrate. Unless one titrates very close to the end point the ferric phytate still interferes somewhat. This necessitates a preliminary determination of the end point by the Heubner (*4*) method. Even so, the determinations give a value of phytin phosphorus which is lower than that obtained with the Heubner method. The authors have modified this Heubner procedure in such a way that this difficulty is entirely removed.

Procedure

Extract an 8-gram sample with 200 cc. of 2.0 per cent hydrochloric acid for 3 hours with occasional shaking and filter through a double layer of hardened filter paper. To a 50-cc. aliquot of this filtrate in a 400-cc. beaker add 10 cc. of a 0.3 per cent ammonium thiocyanate solution and 107 cc. of distilled water (resultant acidity is therefore 0.6 per cent). Add standardized ferric chloride solution (0.001 gram of iron per cc.) from a buret until the typical brown color of ferric thiocyanate no longer appears to be fading, then add 0.25 to 0.50 cc. more. Allow to stand until the precipitate flocculates (10 to 20 minutes) and filter through two layers of hardened filter paper. The flocculation may be induced by occasional stirring. Wash the precipitate with three 11-cc. portions of distilled water.

Make up a blank by adding 10 cc. of 0.3 per cent ammonium thiocyanate and 3.16 cc. of hydrochloric acid (sp. gr. 1.19) to 187 cc. of distilled water. Add ferric chloride solution to the blank until the color matches that of the unknown. Calculate the percentage of phytin phosphorus by the following formula:

$$\text{Per cent of phytin phosphorus} = \frac{\text{cc. of ferric chloride (sample} - \text{blank)} \times \text{grams of iron per cc.} \times 1.19 \times 100}{\text{weight of sample}}$$

The authors are not yet convinced that this 1.19 factor is correct. Tests have shown that the gravity filtration, taking perhaps 1 hour, causes no perceptible diminution of the color.

The advantage of the proposed modification in terms of reduced variability as compared with the original Heubner method is shown by the data in Table I.

Table I. Comparison of Methods

(Corn extract)

Investigator	Ferric Chloride[a] Heubner	Ferric Chloride[a] Harris-Mosher	Phytin Phosphorus Heubner	Phytin Phosphorus Harris-Mosher
	Cc.	*Cc.*	*Gram per 100 grams*	
B. P.	3.59	3.89	0.209	0.227
	3.85	3.88	0.225	0.227
P. K. B.	3.95	3.92	0.230	0.229
	3.55	3.91	0.207	0.228
S. J.	4.03	3.93	0.236	0.229
	3.17	3.91	0.185	0.228
J. M. B.	4.24	3.92	0.248	0.229
	3.61	3.92	0.211	0.229
G. B. A.	3.82	3.87	0.223	0.226
	3.83	3.89	0.224	0.227
	3.94	3.90	0.230	0.227
J. F.	3.91	3.89	0.229	0.227
	3.81	3.88	0.222	0.227
	3.70	3.87	0.217	0.226
	Average		0.221	0.228
	Average deviation		0.011	0.001
	Maximum deviation		0.036	0.002

[a] 0.000965 gram of iron per cc.

Table II demonstrates that this modification is equally applicable to determinations of phytin phosphorus in grains other than corn.

The phytin phosphorus content of pure calcium phytate is 19.7 grams per 100 grams (calculated). The crude sample

included in the determinations in Table II is about 50 per cent pure.

TABLE II. HARRIS-MOSHER METHOD

	Ferric Chloride[a]	Phytin Phosphorus	Sample Used
	Cc.	*Grams/100 grams*	*Grams*
Oats	3.94 3.95	0.228 0.229	2.0000
Barley	3.73 3.75	0.216 0.217	2.0000
Corn	3.80 3.79	0.222 0.222	2.0000
Wheat gluten	3.24 3.23	0.186 0.185	2.0000
Calcium phytate (crude)	4.38 4.40	10.07 10.11	0.05

[a] 0.000965 gram of iron per cc.

There is always a possibility, in colorimetric titrations of plant extracts, that a substance may be present which contributes a color which either masks the true end point or produces a false one. To check this possibility the authors subjected three solutions to the Hardy color analyzer.[1] The results are shown in the figure. Curve A was made by an extract of corn which had been matched with a blank (curve B). The two curves show that the matching of the color with the eye is quite accurate. They also show that the only color which was visible (and therefore used in matching the solutions) was that produced by the ferric thiocyanate. Therefore false end points are absent from the titration.

[1] Description of an early model, *J. Optical Soc. Am.*, **18**, 98 (1928). Description of instrument used for these determinations will appear in the same journal.

A third solution containing a large excess of ferric chloride was also tested (curve C). This curve indicates that at about 420 λ the absorption produced by ferric thiocyanate reached a maximum.

CONCLUSIONS

The Heubner-Stadler method for the determination of phytin phosphorus has been modified by titrating the unknown solution with ferric chloride beyond the end point, filtering, and matching the color of the filtrate with a blank. Determinations are much more accurate because the insoluble colloidal ferric phytate which clouds the end point has been removed.

Color analyses have shown that there is no color of plant origin which interferes with the end point in the titration of corn extracts with this method.

The color produced by ferric thiocyanate reaches a maximum absorption at 420 λ.

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Improved Method for Determination of Percentage Acetyl in Organic Compounds

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A NUMBER of methods have been described in the literature for the quantitative estimation of the percentage acetyl in organic compounds. All these methods consist essentially in first splitting off the acetyl group and then determining quantitatively the acetic acid produced. The various methods described in the literature have been adequately reviewed by Meyer (*2*). Of the more commonly employed methods, mention need only be made in this connection of the method of Wenzel (*6*) and of Perkin (*3*). Wenzel hydrolyzes the substance with slightly diluted sulfuric acid, primary sodium phosphate and metaphosphoric acid being then added and the acetic acid distilled off under reduced pressure. Such a procedure, however, involves as a rule long and tedious operations, and the results are not always reliable, particularly with small quantities of substance. Perkin hydrolyzes the substance with alcohol and concentrated sulfuric acid, distills off the ethyl acetate formed into an excess of 0.5 *N* alkali, saponifies the ethyl acetate, and then determines the excess of alkali. The Perkin method, although relatively simple to carry out, suffers from the disadvantage that charring of the sample by the sulfuric acid may take place with the production of sulfur dioxide which, of course, interferes with the determination. With the technic recommended by Perkin it is difficult to obtain quantitative results, particularly with smaller quantities of material. Sudborough and Thomas (*5*) have used aromatic sulfonic acids such as benzene sulfonic acid or α- and β-naphthalene sulfonic acids. Freudenberg and Harder (*1*) have

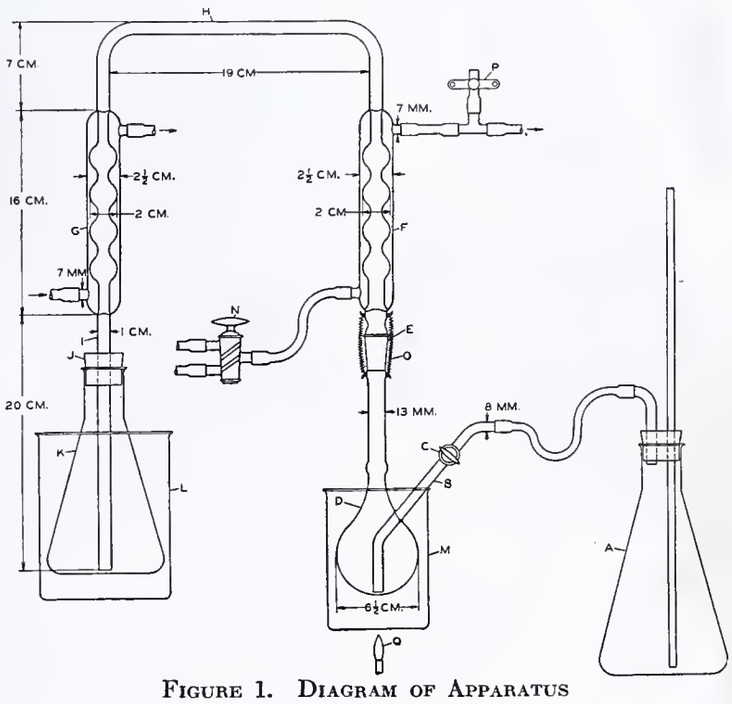

FIGURE 1. DIAGRAM OF APPARATUS

employed *p*-toluene sulfonic acid for breaking up the acetylated compound.

The method described in this paper is a modification of the Perkin method. It has none of the disadvantages of the original method, and is an improvement over the modified procedure employed by Freudenberg and Harder. Using the technic described it has been possible to obtain quantitative results not only with -O-acetyl but also with -N-acetyl compounds.

Apparatus

The apparatus used is illustrated in Figure 1. It is constructed of Pyrex glass and consists of a reaction flask, *D*, which is provided with an inlet tube, *B*, and stopcock, *C*. *D* is placed in water bath *M*, which is heated with microburner *Q*. Connection between *D* and condenser *F* is made through interchangeable ground-glass joint *E* (No. 11) and is held fast by means of springs *O*. Condenser *F* is connected through glass tube *H* to condenser *G*. *K* is a 300-cc. Erlenmeyer flask upon which two marks have been placed indicating a volume of 100 and 150 cc., respectively. During the distillation *L* serves as an ice bath, and during the hydrolysis of the ethyl acetate, as a water bath. *J* is a rubber stopper, the opening of which has been lubricated with glycerol so that it can readily slide up and down tube *I*. *N* is a two-way stopcock through which cold water for condenser *F* is passed. By turning *N* and opening pinchcock *P* it is possible to drain the water immediately from *F*. *A* is a 500-cc. Erlenmeyer flask, partly filled with aldehyde-free 95 per cent ethanol and used for generating alcohol vapor. It is heated by means of an electric hot plate, not shown on the drawing.

Procedure for -O-Acetyl Compounds

The weighed sample (0.3 to 0.4 gram) is placed in reaction flask *D* to which are also added 5 grams of *p*-toluenesulfonic acid,[1] a small piece of unglazed tile, and 25 cc. of 95 per cent aldehyde-free ethanol (prepared by the method of Stout and Schuette, *4*). Into receiver *K*, 25 cc. (accurately measured with a pipet) of an alcoholic potassium hydroxide solution (approximately 0.2 *N*) and a small piece of unglazed porcelain are put. *J* is moved up close to the inner seal of *G*, leaving *K* open to the atmosphere. *K* is surrounded with crushed ice contained in *L*, which is supported by means of a ring and stand. The height of the ring is so adjusted that *I* reaches close to the bottom of *K*. *E* is lubricated with stopcock grease and is attached to *F* with springs, *O*. Cold water is circulated through both condensers, and *D* is placed in water bath *M*, and the reaction mixture is refluxed for 15 minutes. The water in condenser *F* is then drained, stopcock *C* is opened, and a slow stream of alcohol vapor is allowed to pass into *D* from generator *A*. This operation is continued until the total volume in *K* measures 150 cc.

During the distillation, *M* is heated with microburner *Q* at such a rate that at the end of the distillation the volume in *D* is reduced approximately one-half. *K* is then lowered so that the end of *I* is above the level of the liquid. Stopcock *C* is shut off, and the rubber tube attached to generator *A* is disconnected from *B*. *D* is detached from *F*, and *J* is lowered until it is approximately 2 inches (5 cm.) from the lower end of *I* and is securely attached to *K*. The ice in *L* is replaced with hot water, and the distillate is refluxed for one-half hour. During this period *L* is heated with a microburner. *K* is then disconnected, diluted with distilled water, and the unused potassium hydroxide determined by titration with 0.1 *N* acid, phenolphthalein being used as the indicator.

A somewhat sharper end point is obtained by running in a known excess of 0.1 *N* acid and determining this excess by titration with 0.1 *N* alkali. A blank determination is made following the procedure above described, except that no sample is added to *D*. From the blank determination the normality of the alcoholic potassium hydroxide solution is accurately determined. The number of cubic centimeters of 0.2 *N* potassium hydroxide solution used when multiplied by 0.86 and divided by the weight of the sample gives the percentage acetyl in the compound.

Procedure for -N-Acetyl Compounds

The analytical procedure described above is modified as follows:

[1] This is purified as follows: A strong aqueous solution of *p*-toluenesulfonic acid is placed in a distilling flask which is attached to a condenser, and a current of steam passed through the solution until the distillate coming over no longer reacts acid. The residual solution of the sulfonic acid is concentrated on the steam bath and allowed to crystallize. The crystals are filtered off and dried in a vacuum desiccator over sulfuric acid.

Instead of refluxing the solution in *D* for 15 minutes, it is refluxed for 2 hours. The water in condenser *F* is then drained, and alcohol vapor from generator *A* is allowed to pass through the solution contained in reaction flask *D*. This operation is continued until the volume of the solution in *K* measures 100 cc. During this distillation the heating of *M* is so regulated that the volume of the reaction mixture in *D* is reduced one-half. *C* is then shut off, and cold water is again circulated through *F*. The solution in *D* is then refluxed for 30 minutes, after which the cold water circulating through *F* is shut off, the jacket of the condenser *F* is drained, and a current of alcohol vapor from *A* again passed through the solution in *D*. This operation is continued until the volume of the liquid in *K* measures 150 cc. The refluxing of the solution in *K* and the determination of the excess of potassium hydroxide solution are carried out exactly as described above for -O-acetyl compounds.

The results obtained with several -O-acetyl compounds and with acetanilide are given in Table I.

Table I. Determination of Acetyl

Compound	Weight of Sample	0.2 *N* KOH Used	Acetyl Found	Acetyl Calculated
	Gram	*Cc.*	%	%
β-Naphthyl acetate	0.4000	10.87	23.3	23.1
β-Naphthyl acetate	0.4000	10.88	23.3	23.1
β-Naphthyl acetate	0.2000	5.35	23.0	23.1
Diacetyl toxicarol	0.3000	5.95	17.05	17.4
Acetyl dehydrotoxicarol	0.3500	3.90	9.58	9.56
Cellobiose octaäcetate	0.2000	23.9	51.3	50.74
Acetanilide	0.3500	13.1	32.1	31.8
Acetanilide	0.3500	13.08	32.1	31.8

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Suction Device

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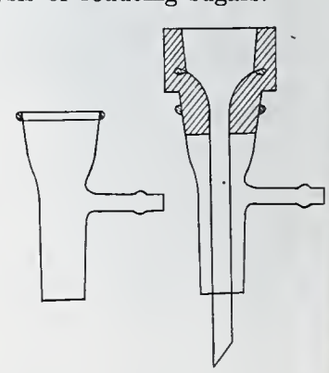
In laboratory filtrations employing suction, it is frequently desired to introduce the filtrate directly into the Erlenmeyer or any other flask. For such a purpose, the piece of apparatus shown in the illustration as used with a Walter crucible holder has proved convenient. This device is particularly applicable in the analysis of reducing sugars.[1]

The apparatus may be readily constructed from a Pyrex test tube, by attaching a side arm at a convenient distance from its mouth, expanding the mouth to fit a Walter crucible holder, and cutting the test tube at a convenient distance from the bottom, to allow a portion of the holder stem to extend beyond the so-called suction funnel stem.



Received June 9, 1934.

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Analysis of Dry Refinery Gases below Pentane by Simple Batch Distillation

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A method of calculating a master graph, whereby the composition of a refinery gas may be determined from an ordinary simple distillation of the condensed gas, has been developed. A computed graph is presented for the range commonly encountered, but limited to dry gases containing no compounds of higher boiling point than butanes. The method can be applied, if desirable, to more complex mixtures.

The preparation of a master graph in the manner outlined is believed to be as satisfactory for routine work as the correlation obtained by experimental distillation curves of synthetic mixtures according to the procedure presented by Robertson and Rosen (6). Moreover, since the calculated graph may be based on the particular close-boiling hydrocarbons actually present in the gas, instead of synthetic mixtures of pure paraffin hydrocarbons, the application of the graph is greatly facilitated. For approximate analysis, no correction factor is necessary.

THE use of fractionation for analysis of gases and gasolines has come into extensive use in the oil industry during recent years. The most widely used type of apparatus utilizes the principle of rectification in a packed column with controlled countercurrent contact between vapor and reflux. Apparatus of this type has been described by Podbielniak (5), Oberfell and Alden (4), Schaufelberger (7), and Davis and Daugherty (2). This method gives very accurate results, but requires the services of a skillful operator. Furthermore, the apparatus is expensive and its operation requires considerable time. The advantage of a method which would not present these difficulties is obvious.

Simple batch distillation of a condensed gaseous mixture without fractionation has been used for refinery gas analysis in a method described by Robertson and Rosen (6). Before the distillation of the condensed sample, methane and "fixed gases" are pumped off. A good separation between methane and the heavier components at the temperature of liquid air is possible under conditions described in the above-mentioned article, without fractionation. The gas sample remaining, which must be free of pentanes and heavier, is distilled at atmospheric pressure and a curve is obtained analogous to the ordinary A. S. T. M. distillation curve for petroleum products. The material distilled consists of a mixture of three close-boiling fractions of hydrocarbons containing two, three, and four carbon atoms per molecule. From the distillation curve, aided by a master graph previously prepared by distillation of mixtures of ethane, propane, and normal butane, the composition of the sample is obtained. In applying the distillation data to the master graph it is necessary to use an empirical correction factor, since ordinary refinery gas contains unsaturated and branch chain compounds in addition to normal paraffin hydrocarbons.

This short-cut method of analysis possesses numerous features which make it valuable for routine work. A skilled operator is unnecessary to run the apparatus, the method is simple and rapid, and only a small quantity of liquid air is required. Its use in connection with a master graph is limited to four-component mixtures, and therefore to analysis of dry gases, such as would be rejected from absorption plants and high-pressure stabilizers at refineries.

The object of this paper is to present a further simplification of the short-cut method, making it more readily applicable to refinery work. In order to reduce the amount of preliminary experimental work required to construct a master graph, a mathematical correlation between the fractional distillation of hydrocarbon mixtures and the short-cut method of simple distillation has been developed, by means of which it is possible to construct a master graph based on the data furnished from a single Podbielniak analysis of a typical gas in the desired range.

Method of Computation

The computation of the separation possible in any given case of simple distillation without fractionation was first made by Lord Rayleigh. Walker, Lewis, and McAdams (8) present a special form of the Rayleigh equation which applies to any two components of a multicomponent mixture if these two follow Raoult's law. The assumptions involved in arriving at this equation parallel very closely the conditions which exist during the operation of the short-cut apparatus designed by Robertson and Rosen (6). The mathematical derivation, as applied to the case in hand, follows:

Nomenclature

E = moles of "ethanes" present in the liquid residue at any time
P = moles of "propanes" present in the liquid residue at any time
B = moles of "butanes" present in the liquid residue at any time
V = vapor pressure of any constituent
dE = moles of "ethanes" evaporated at any instant
dP = moles of "propanes" evaporated at any instant
dB = moles of "butanes" evaporated at any instant
p = partial pressure exerted by any constituent in the liquid residue
α = relative volatility, ratio of the vapor pressures of any two constituents

Subscripts

1, 2 = initial and final conditions
E, P, B refer to "ethanes," "propanes," and "butanes"

It will be assumed that the three close-boiling fractions, containing two, three, and four carbon atoms in each hydrocarbon molecule, respectively, behave as pure components throughout the distillation. They will be designated as "ethanes," "propanes," and "butanes" for convenience. For any given temperature each fraction will have a definite vapor pressure, which will vary with temperature in the same way as the boiling point of the nearest pure hydrocarbon.

If it be assumed that the vapor evaporated from the sample is removed as fast as it is produced, and that it obeys the perfect gas laws,

$$\frac{-dE}{-dP} = \frac{p_E}{p_P} \qquad (1)$$

The validity of Raoult's law as a good approximation for the behavior of hydrocarbon mixtures at low temperatures is quite generally accepted. If this law holds, the following relationships obtain:

$$p_E = V_E\ E/E + P + B$$
$$p_P = V_P\ P/E + P + B$$

$$\frac{p_E}{p_P} = \frac{V_E E}{V_P P} = \alpha_{EP}\ \frac{E}{P}$$

Substituting in Equation 1,

$$\frac{-dE}{-dP} = \alpha_{EP}\ \frac{E}{P} \qquad \frac{-dE}{E} = \alpha_{EP}\ \frac{-dP}{P}$$

If the deviation from Raoult's law were known, a correction factor could readily be applied to the relative volatility in the above equation. The equation may be integrated directly if the value of α_{EP} does not change,

$$\log \frac{E_1}{E_2} = \alpha_{EP} \log \frac{P_1}{P_2} \qquad (2)$$

Similarly,

$$\log \frac{P_1}{P_2} = \alpha_{PB} \log \frac{B_1}{B_2} \qquad (3)$$

The value of α will remain constant, strictly speaking, only for a constant-temperature batch distillation. For constant-pressure distillations where the initial and final temperatures vary little, a good approximation may be obtained by using the average temperature.

Preparation of Master Graph

An inspection of these equations shows that the only information necessary to correlate the fractional analysis of a given mixture with its simple distillation is an accurate vapor pressure–temperature plot. The plot used in this work is the one recently published by Copson and Frolich (*1*).

The average boiling points of the ethanes, propanes, and butanes fractions were obtained by actual calculation from several Podbielniak analyses of the types of gases under consideration—i. e., cracked refinery gases containing no pentanes or heavier. The boiling points were as follows: ethanes, −90.0° C.; propanes, −44.5° C.; butanes, −5.0° C. It is believed that these boiling points are fairly representative of ordinary refinery gas analysis.

The correlation between the composition of the condensed gas distilled, which is a three-component mixture, and the distillation curve obtained is based on the fact that the determination of any two independent properties of a ternary mixture, in this case two boiling points on a distillation curve, is sufficient to fix the composition of the mixture. The points selected in this case were the 20 and 70 per cent points. Theoretically any other points would do just as well. From a practical standpoint, however, it is difficult to duplicate the first and last 10 per cent of any distillation curve. Furthermore, since the accuracy of this method depends on the determination of two clearly defined residue compositions, it is obvious that the faster the boiling temperature, and therefore the composition, is changing with respect to percentage distilled off at the points selected, the more closely will the two compositions and therefore the desired analysis be fixed. This condition is met by selecting points on the distillation curve which correspond roughly to the average percentage composition of the liquid components (for this case 20 per cent ethanes, 50 per cent propanes, 30 per cent butanes).

Several short-cut analyses indicated that the average boiling temperature from the initial to the 70 per cent point was about −50° C. The relative volatilities of ethanes to propanes (α_{EP} = 7.44) and of propanes to butanes (α_{PB} = 6.62) used in making computations from Equations 2 and 3, respectively, are calculated for this temperature and used as constants in all computations involved in preparing the master graph. Greater accuracy could, of course, be obtained by varying the relative volatility with the boiling point.

The temperatures calculated at the two chosen percentages off are plotted against each other on ordinary graph paper. Lines are drawn through all points having the same concentration of one component and another set of lines drawn through all points having the same concentration of another component. A graph showing these two sets of lines is sufficient to define any composition of the ternary mixture for the range covered.

The detail of the calculation is facilitated by making use of the fact that the equation relating propanes to ethanes must be a straight line on log-log paper with a slope equal to the relative volatility (α) of these two fractions. The original composition of the sample distilled determines this line. Similarly, a line may be drawn on the same graph for propanes and butanes. By means of these two plots the composition of the material remaining in the distilling bulb at any percentage off may be calculated by trial and error, making use of the fact that the sum of the percentages read from the plots must add up to the percentage of residue remaining in the distilling bulb. The boiling point of the liquid residue is obtained by multiplying the mole per cent of each component by the vapor pressure of the pure component at a temperature which is assumed to be near the expected boiling point. The sum of the partial vapor pressures so obtained is divided by 100 to obtain the total vapor pressure of the liquid at the assumed temperature. By several trials the temperature corresponding to one atmosphere, the pressure at which all the analytical distillations are conducted, may be obtained.

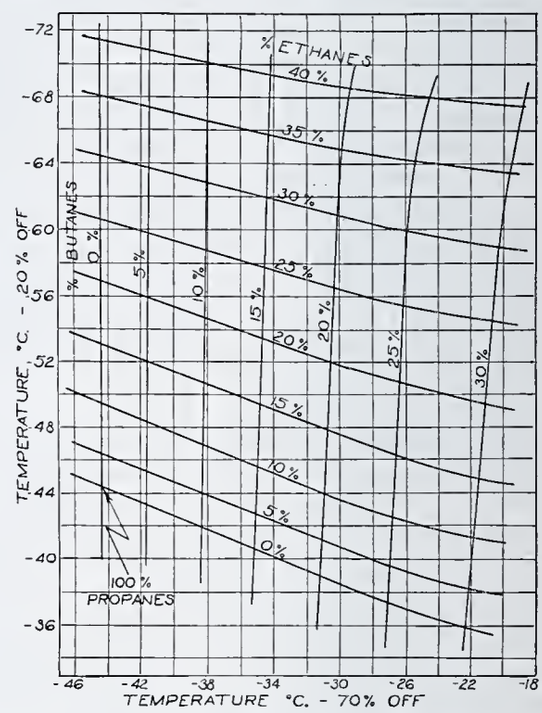

Figure 1. Master Graph for Refinery Gases

The master graph presented (Figure 1) was constructed from 63 calculated points, one for each intersection shown on the plot. The effort involved in the construction of such a plot is much smaller than would be required to make synthetic mixtures and obtain actual data on their distillation characteristics. It is possible to compute the two selected

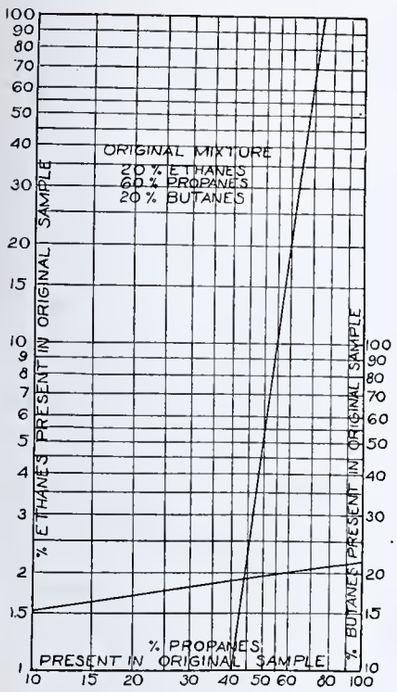

FIGURE 2. CHANGE IN COMPOSITION DURING SIMPLE DISTILLATION

boiling points for about twenty theoretical mixtures in a working day.

The following examples show in detail how a typical point on the master graph is calculated and how the graph is used:

ILLUSTRATION 1. It is desired to determine the 20 and 70 per cent points for a gaseous mixture containing 20 per cent ethanes, 60 per cent propanes, and 20 per cent butanes.

The plot, Figure 2, is constructed on log-log paper. The line representing ethanes *vs.* propanes has a slope of

$$\alpha_{EP} = \frac{V_E \text{ at } -50° \text{ C.}}{V_P \text{ at } -50° \text{ C.}} = \frac{4410 \text{ mm.}}{593 \text{ mm.}} = 7.44$$

It passes through the point ethanes = 20, propanes = 60. Similarly, the line representing propanes *vs.* butanes has a slope of

$$\frac{1}{\alpha_{PB}} \times \frac{V_B \text{ at } -50° \text{ C.}}{V_P \text{ at } -50° \text{ C.}} = \frac{89.7 \text{ mm.}}{593 \text{ mm.}} = \frac{1}{6.62}$$

This line passes through the point propanes = 60, butanes = 20.

The two lines on Figure 2 numerically represent the percentage at any time of the amount of each component present at the beginning of the distillation. The sum of the percentages of ethanes, propanes, and butanes must add up to the percentage residue remaining at any time during the distillation.

In order to calculate the 20 per cent point, the percentage of any component in the desired residue is guessed. This assumption enables the computation of the percentages of the other two components by means of Figure 2. If the three percentages so determined add to 80.0, the first assumption is correct. By successive approximations, it is possible to arrive rapidly at the following value for the residue composition in terms of 100 parts of original sample:

C_2 =	7.6
C_3 =	52.7
C_4 =	19.7
	80.0 parts of residue

It is unnecessary to convert this composition to a basis of 100 parts of residue in order to determine its boiling point. The sum of the partial pressures at the assumed temperature must in this case add to 608 mm. (0.8 atmosphere) instead of 760 mm. (1 atmosphere). Since the composition of the sample is always given in volume per cent, which in the case of a gas is interchangeable with mole per cent, no conversion factors are necessary to reduce the composition of the residue to mole per cent before making the boiling point calculation.

	Vapor Pressure At −53° C. *Mm.*		Mole Fraction		Partial Pressure *Mm.*
C_2	3960	×	0.076	=	301
C_3	517	×	0.527	=	272
C_4	74	×	0.197	=	15
					588
	At −52° C.				
C_2	4110	×	0.076	=	312
C_3	540	×	0.527	=	285
C_4	80	×	0.197	=	16
					613

By interpolation the value at which the sum of the computed partial pressures is 608 mm. is −52.2° C.

In order to calculate the 70 per cent point on the distillation curve, a similar procedure is followed. Since extrapolation of the ethanes-propanes line, not shown on the plot, shows the value of ethanes to be less than 0.001 per cent, to obtain the composition of the residue it is only necessary to select such a value for propanes on the propanes-butanes line, that the sum of the propanes and butanes is 30.

C_3 =	13.9
C_4 =	16.1
	30.0

The boiling point is found by trial and error as before, except that in this case the sum of the partial pressures must add to 228 mm. (0.3 atmosphere).

	Vapor Pressure At −30° C. *Mm.*		Mole Fraction		Partial Pressure *Mm.*
C_3	1370	×	0.139	=	191
C_4	262	×	0.161	=	42
					233
	At −31° C.				
C_3	1323	×	0.139	=	184
C_4	251	×	0.161	=	40
					224

The boiling point by interpolation at 70 per cent off is −30.5° C.

ILLUSTRATION 2. A certain dry gas is drawn at barometric pressure into the sampling bulb of the short-cut apparatus. The sample is condensed, and all fixed gases and methane are pumped off at liquid air temperature. The sample is subsequently distilled, according to the Robertson and Rosen (*6*) method. The analysis of the gas is desired.

DATA (RUN 3)

Pressure in receiver at end of distillation	471.0 mm.
Pressure in receiver after equalization with distilling bulb (P_2)	476.8 mm.
Temperature at 20 per cent point (at 0.20 × 471 = 94.2 mm.)	−60.5° C.
Temperature at 70 per cent point (at 0.70 × 471 = 329.7 mm.)	−22.5° C.
Volume of sampling bulb	501 cc.
Volume of distilling bulb + lines + receiver bulb	527 cc.
Barometric pressure	768.6 mm.

The pressure in the apparatus after equalization, if no methane and fixed gases had been removed, would be represented by:

$$P_1 = \frac{\text{volume measured} \times \text{atmospheric pressure}}{\text{volume of distillation bulb + lines + expansion bulb}}$$

$$P_1 = \frac{501 \times 768.6}{527} = 731 \text{ mm.}$$

The difference between P_2 and P_1 represents the pressure due to fixed gases and methane pumped off before the distillation is begun. Its fraction of the total pressure, P_1, gives the percentage of fixed gases and methane in the sample.

$$731 - 476.8 = 254.2 \text{ mm.}$$

$$\frac{254.2}{731} \times 100 = 34.8 \text{ per cent methane}$$

The composition of ternary mixture distilled is determined by use of the chart, Figure 1.

C_2	31.3%	
C_4	27.9%	
C_3	40.8%	by difference
	100.0	

A mixture of this ternary gas with 34.8 per cent methane and fixed gases gives the analysis of the gas sample.

C_1	34.8
C_2	20.4
C_3	26.6
C_4	18.2
	100.0

DISCUSSION OF PROCEDURE

The apparatus and procedure used are entirely similar to those developed by Robertson and Rosen with several minor modifications. Since the master graph was to be computed from entirely independent vapor pressure data obtained from the literature, it was necessary to calibrate the thermocouple used to measure liquid temperatures very accurately. In order to avoid superheating of the liquid which does not boil rapidly during the removal of methane or the subsequent distillation, it was found advantageous to introduce a small quantity of finely powdered silicon carbide into the distilling

bulb. According to Midgley (*3*), this material is very effective as a boiling stone.

The fact that the vapors, after boiling from the liquid, immediately come in contact with the relatively hotter walls of the distilling bulb prevents their partial condensation. In consequence, the distillation of condensed gases parallels a simple batch distillation without fractionation much more closely than the ordinary A. S. T. M. distillation, in which the temperature of the walls of the distilling bulb above the boiling liquid is below its dew point. There are, however, certain details in which the experimental procedure does not exactly follow the mechanism assumed in the calculation.

The separation of methane from the ternary mixture involves the loss of a certain amount of ethylene from the ethanes fraction. This would tend to depress the front end of the curve. Moreover, the distillation curve is constructed from readings of the increase in pressure of the overhead gas in a receiving bulb, and therefore represents the percentage of the material finally recovered in the receiver. The graph, however, is constructed on the basis of per cent evaporated from the condensed sample in the distilling bulb. An error is, therefore, introduced by the amount of gas which fills the distilling bulb at atmospheric pressure, before any sample is collected. Furthermore, a lag exists in the thermocouple readings. These conditions, in addition to the approximate nature of the assumptions made in calculation of the master graph will cause discrepancies between the predicted and observed analyses.

Application of Method

Several typical analyses of dry refinery gases are presented in the accompanying table for comparison with the fractional distillation method. These gases are derived at 25 per cent from crude still operation, 25 per cent from vapor phase cracking in a DeFlorez unit, and 50 per cent from liquid phase cracking in Cross units.

	Run 1		Run 2		Run 3	
Constituent	Podbielniak	Short cut	Podbielniak	Short cut	Podbielniak	Short cut
Fixed gas and methane	39.4	38.2	1.3	1.1	36.5	34.8
Ethanes	24.0	23.2	10.5	12.0	18.0	20.4
Propanes	25.4	28.1	56.1	57.2	24.8	26.6
Butanes	11.2	10.5	32.1	27.9	20.7	18.2

The reasons for this inconsistency are believed due as much to variations from day to day of the composition of the close-boiling fractions contained in the refinery gases and to errors in experimental observation as to the inadequacy of theoretical treatment.

The data on hand at present indicate that the percentages of ethanes predicted from the master graph are about 2 per cent too high. Likewise, the butanes predicted are about 2 per cent lower than actually obtained in a fractional analysis. Since the accuracy with which the analyses may be performed is not much greater than this deviation, no correction has been incorporated into the master graph. When sufficient data become available to establish definitely this trend of deviation, it may be readily taken into consideration by changing the relative position of the constructed "grid" and the coördinates of Figure 1.

While not as accurate as the best fractional distillation analysis, the short-cut method with the simplification presented is well adapted to routine analysis for plant and laboratory. The method of preparing a master graph indicated above is believed to be quite as satisfactory for this type of work as that based on experimental data for synthetic mixtures of pure paraffin hydrocarbons, and presents the advantage of an appreciable saving of time and expensive chemicals. It is planned to extend the application of the Rayleigh equation to mixtures containing pentanes. This would make the correlation applicable, not only to dry gases, but to practically all but the heaviest refinery gases.

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Self-Filling Pipet for Dispensing Hot Caustic Solutions

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Bureau of Plant Industry, Austin, Texas

An ordinary pipet modified as shown in Figure 1 greatly facilitates manipulation of the hot ferric sulfate–sulfuric acid solution used in the permanganate method for determining copper reduced in the various methods of sugar analysis. For this specific purpose, the lower tube of a 50-cc. pipet was cut off near the bulb and the new outlet fire-polished until the opening was of suitable size (about 3 mm.). The bends in the upper tube were easily made after heating with an ordinary wing-top burner.

The 50-cc. pipet operates satisfactorily when the solution is contained in a 2-liter Pyrex beaker which can conveniently be heated by means of a small electric hot plate. The pipet is placed in the solution in a position similar to that shown by the dotted lines. It sinks gradually as the bulb fills and eventually assumes the position shown in solid line. The latter position permits removal of a large proportion of the liquid in the beaker before refilling is necessary. When the liquid is to be dispensed, the filled pipet is best twisted so the bulb is vertical. When dissolving cuprous oxide which has been collected on an asbestos mat in a Gooch crucible, it is convenient to loosen the mat with a pointed glass rod, transfer the bulk of it to a 250-cc. beaker, and finally wash down the inside of the crucible with the stream of hot acid solution from the pipet.

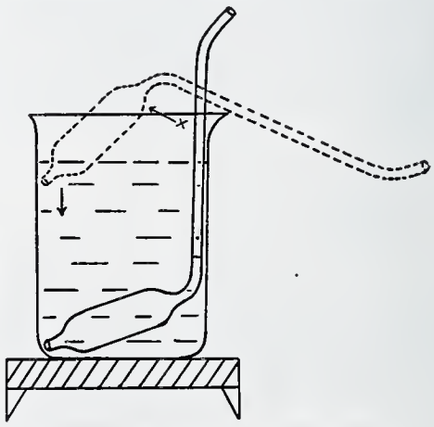

Figure 1. Self-Filling Pipet

If such a pipet were to be made specially to deliver a more exact and predetermined volume of liquid, it would undoubtedly be desirable to attach the upper tube near point *X* since air bubbles tend to collect there when the level of liquid in the beaker becomes low.

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Preparation of Samples for Determination of Arsenic

Oxygen-Bomb Combustion Method

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In the course of a clinical investigation of persons observed to be habitually excreting arsenic in their urine, especially with respect to certain cases exhibiting disturbances suggestive of chronic poisoning through the action of arsenic in the tissues of the nervous system, it became important to study the possible existence of sources from which arsenic might gain direct access to the central nervous system by way of the nasal tract. This study led to the examination of many specimens of the finely particulate and air-suspensible materials to which most city dwellers are directly exposed in the course of their daily lives. Such substances include sedimentary house dusts, as represented by the powdery portion of the material ordinarily collected by a household vacuum cleaner, and those finer particles of dust and soot of the inside and outside atmosphere which are obtainable by methods of filtration from the air.

A report on this study will be published elsewhere (*16*), but we are here concerned only with analytical methods. The quest which led to the development of the method to be described was not directed towards the estimation of arsenic in food materials, but primarily towards the better detection of minute quantities of arsenic in biological specimens as well as in house and atmospheric dusts. For these purposes it became highly desirable to devise an analytical method which would be capable of relatively rapid, simple, and inexpensive performance, and which would give reliable results in the detection of organically bound arsenic in any form. The examination of other materials such as foodstuffs has been included in the series here reported in order to show the general scope of usefulness of the method.

Methods of acid digestion with heat, as usually employed in preparing organic substances for the determination of arsenic in the Marsh or Gutzeit apparatus, are not only slow, laborious, and productive of corrosive fumes, but the results have frequently been questioned (*6–13*) on the basis of the possible volatilization of at least a portion of the arsenical content in the form of higher molecular arsines. This same objection holds with the well-known chlorate method of Fresenius and Babo, the perchloric acid method of Noyes and Bray (*11*), or the $MgO{\cdot}Mg(NO_3)_2$ oxidation of Kohn-Abrest (*8*), all of which employ digestion in open receptacles at boiling temperature, as well as with air-combustion methods in ignition tubes (*12*).

Numerous references (*5*, *7*, *10*) may be cited, questioning the validity of findings on the ground of contamination of the specimens by reagents employed during preparation or testing, or by exposure to possible contamination from atmospheric dust or laboratory apparatus. It is therefore desirable to employ reagents in which freedom from arsenic is not only generally conceded but readily demonstrable, and still further to avoid criticism on this ground by using relatively small amounts of a few reagents. The proportion, by weight, of reagents to samples ranges high in all acid-digestion methods, especially when supplemented by repeated adsorptions of residues by means of precipitated adsorbents, as ferric ammonium sulfate (*5*). In such processes lengthy exposure in open vessels of residues and of adsorbents to atmospheric dust contamination is an important source of error.

The method of bomb combustion using pure oxygen was first devised by Berthelot (*1*) in 1899. In 1903 Bertrand (*2*) reported its successful use in the determination of small amounts of arsenic in organic matter. Both of these chemists employed a platinum bomb and ignited the charge by means of a small fuse of gun cotton; they took no cognizance, however, of the loss of arsenic in the form of finely divided oxide dispersed in the combustion gases, and these gases were allowed to escape from the bomb untreated.

Early in their investigation the authors became convinced that the complete extraction of suspended particles of arsenious oxide from combustion gases was an essential requirement in developing an adequate method. Preliminary experiments indicated that the loss assignable to this cause varies widely with the nature of the substance burned and the details of the technic employed in its combustion.

Table I. Variation in Arsenic Loss

Lab. No.	Arsenic Content of Sample: Ash only	Arsenic Content of Sample: All products of combustion
	P. p. m.	*P. p. m.*
117	10	20
99	3	12
102	22	30
120	16	17
467	28	28.6

The arsenical content of the smoke resulting from the explosion of some of the substances examined was found to be present in such a finely divided state that its recovery by ordinary methods was impossible except with a long series of Liebig or Geissler bulbs. The opinion was expressed to one of the authors (H. S. S.) by an authority on electrostatic precipitation[1] that a cloud precipitation would probably be more easily applicable to the problem and quite as effective as an electrostatic precipitation, such as that provided by the apparatus of Drinker and Thomson (*3*). This was found to be true.

The preparation, by desiccation, of the material to be burned in oxygen under pressure is not difficult, but certain precautions against volatilization losses are necessary. The means of ignition, as provided in oxygen bombs of approved type, involve no difficulty. In the selection of an oxygen bomb it is obviously important to have the surfaces which are exposed to the flame and to the gases of combustion composed of material which is absolutely resistant to the products of combustion. In this respect lined bombs, either of metal or porcelain, have been found less satisfactory than those of solid construction. It is also desirable to have the valve stem and the passages through which the gases of combustion are exhausted to the washing train, not only of noncorrodible material, but of simple design and readily accessible to washing. To meet these qualifications a bomb cover was designed, the details of which are shown in Figure 1, *A*. Although pressures are safely controlled by a reduction valve on the oxygen line, it is also advisable to place the

[1] The authors are indebted to F. G. Cottrell for his opinion on this subject.

switch which closes the ignition circuit some distance from the bomb, thus eliminating any possible risk to the operator. Although the ordinary fusible nichrome wire of 34 B & S gage has been usually employed by the authors, it was found practicable to use a nonfusing platinum wire to ignite the charge. (While the work here reported has been done with electrical ignition in a rather capacious bomb, it is hoped that an oxygen bomb of smaller capacity can be developed which will be adapted to ignition of the charge by simple conduction of heat.)

biological specimens requires special precautions which are not discussed here.

Where the heat of combustion is small, it has been found advantageous to line the small combustion crucible with arsenic-free cotton gauze. The weighed sample is placed in the bomb and the ignition wires are connected in the usual manner; the bomb is then closed and oxygen is admitted to a pressure between 20 and 30 atmospheres through a pressure-reducing valve connected with the oxygen supply. The charge is then ignited by closing a switch which is preferably situated at some distance from the bomb.

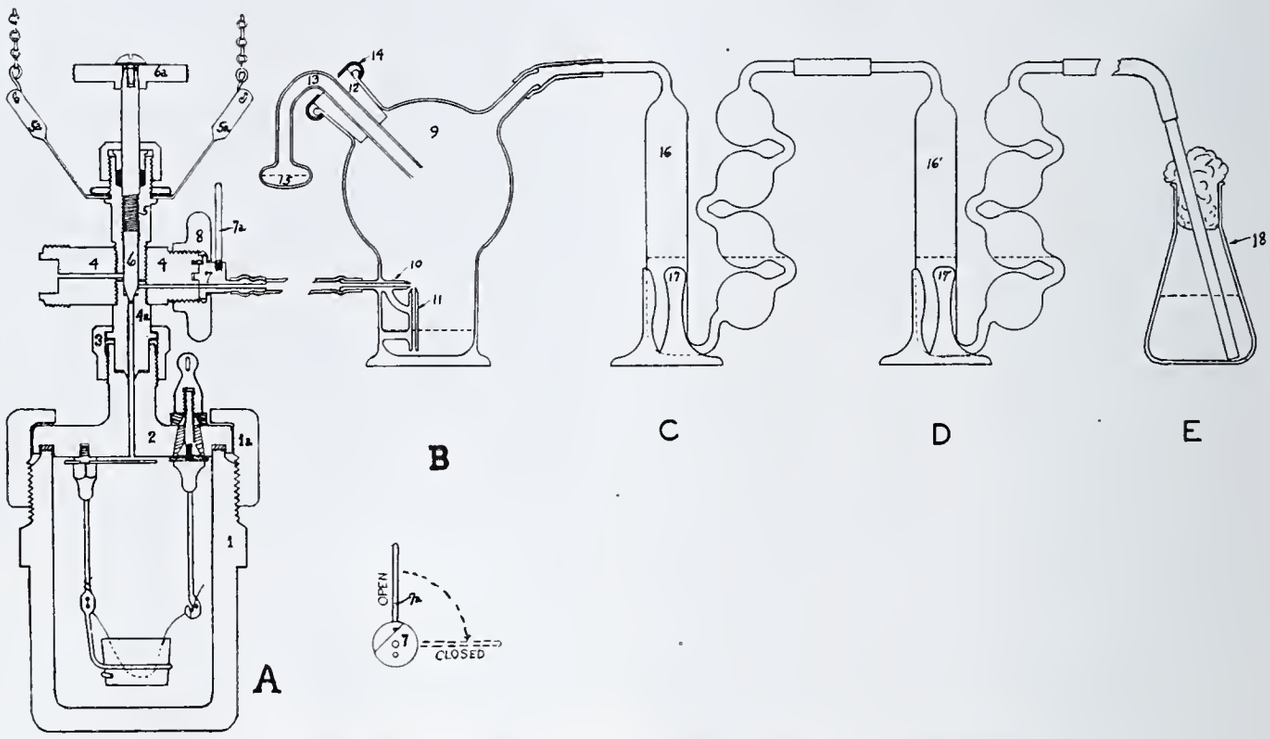

FIGURE 1. CLOUD-PRECIPITATION APPARATUS FOR OXYGEN-BOMB COMBUSTION ANALYSIS

A. Bomb *B.* Cloud-precipitation chamber and nebulizer *C, D.* Koeninck bulbs *C, D, E.* Washing train

The bomb combustion method finally evolved combines a specially designed nebulizing and cloud-precipitating chamber, *B*, with two or more Koeninck gas-washing tubes in series, *C, D*. In this nebulizer the combustion gases enter as a fine jet which sprays hydrochloric acid, producing an ammonium chloride cloud within the chamber by reaction with ammonia. This cloud of ammonium chloride vapor acts as a precipitating agent upon the finely particulate combustion products and facilitates extraction by the washing train.

With this arrangement the reagents employed are such as may be easily obtained in a pure state and are few in number—namely, nichrome (or platinum) wire, hydrochloric acid, ammonium hydroxide, sulfuric acid, oxygen, and water, and the quantities of the first four are very small. The sample is heated only while confined in the bomb, so that losses by volatilization during the oxidizing process are most surely prevented. The quantity of acid introduced into the Gutzeit or Marsh apparatus is only that used in the gas-extraction train and is therefore under close control. This avoids the error affecting quantitative determinations ascribed by Lawson and Scott (*9*) to differences in the rate of evolution of the arsine caused by variations in acid concentration.

METHOD

The sole primary requisite is that the sample be readily combustible. Specimens of high moisture content should be dehydrated, preferably at low temperatures, and for a bomb capacity of 380 ml. as here illustrated, from 0.5 to 1 gram of the dried material is taken. The preparation of certain

The combustion gases are passed into the nebulizing chamber, *B*, by opening first the cut-off valve, 7, and then the needle valve, 6. The passage of the combustion gases through jet 10 produces a spray of hydrochloric acid (1 to 1), which is controlled by operation of the needle valve. This spray causes a simultaneous precipitation of an ammonium chloride cloud by reaction with the ammonia vapor derived from the ammonium hydroxide reservoir, 15, in the tubulature of the chamber. The resulting vaporous mixture is carried through the train of Koeninck bulbs containing a measured amount of sulfuric acid (1 to 3). The residual gases are then washed out of the bomb into the train by first closing the cut-off valve, 7, on the bomb and repeatedly introducing 2 to 4 atmospheres of oxygen and washing through.

The bomb is next opened, the valve passages and bomb are washed with water, and the ash, washings, and solutions from the absorption train are introduced into the Gutzeit generator.

RESULTS

Over six hundred samples have been examined by this method, but many were not appropriate for use as check samples, principally because of difficulties in obtaining true duplicates. Table II shows the results obtained on a wide variety of specimens by the nitric-sulfuric acid digestion method of Gautier as modified by Sanger and Black (*14*), in comparison with the method of the authors.

It seems evident that no paralleled series for comparison by recovery of known amounts of arsenious oxide added to organic materials, as used by Sanger and others (*5, 9*), can be a criterion as to the adequacy of different methods, since the discrepancies between the methods may be attributed to loss of the organically linked arsenical content.

By the method of comparison which the authors have

adopted, employing identical samples of unknown arsenical content, there is always the possibility of nonuniformity of the supposedly identical samples, although an effort has been made to choose for such comparative tests materials which tend to minimize this chance. Conclusions should therefore be drawn only with respect to parities or disparities which show an average consistency or an average tendency in one direction.

Table II. Comparison of Arsenical Contents

Lab. No.	Material	Method: Bomb combustion	Method: Acid digestion
		P. p. m.	*P. p. m.*
531	Soot from kitchen exhaust fan	46	46
506–7	Atmospheric dust[a]	292	186
547	Atmospheric dust	286	209
552–3	Atmospheric dust	231	208
99	Vacuum cleaner dust[b]	12	5
102	Vacuum cleaner dust	30	12
108	Vacuum cleaner dust	30	12
117	Vacuum cleaner dust	20	10
120	Vacuum cleaner dust	17	8
137	Vacuum cleaner dust	33	20
138	Vacuum cleaner dust	53	53
405	Vacuum cleaner dust	40	20
402	Vacuum cleaner dust	80	25
449	Vacuum cleaner dust	36	15
409	Vacuum cleaner dust	25	10
430	Vacuum cleaner dust	45	20
140	Vacuum cleaner dust	25	27
119	Swept dust from cellar floor	360	200
474	Animal hair	8	1
476	Cotton fiber	4	0.5
495	Animal hair	12.5	2.5
462	Cigar tobacco	12	3
475	Pipe tobacco	1	0.0
479	Pipe tobacco	18	2.5
480	Pipe tobacco	40	6.5
459	Pipe tobacco	14	0.0
157	Cigarette[c]	2.5	0.0
582	Cigarette	10	8
591	Cigarette	17	3.3
592	Cigarette	5.7	6
593	Cigarette	10	5.3
596	Cigarette	3.2	1.3
603	Cigarette	20	2.5
620	Cigarette	9.5	1.5
621	Cigarette	9	3.3
502	Canned vegetable	10.3	0.6
504	Egg yolk	9.2	2.1
574	Cocoa	3.6	3.9
612	Coffee	0.5	0.08
613	Processed coffee	1.3	0.0
626	Milk	0.19	0.05
627	Milk	0.15	0.00
628	Milk	0.15	0.00
629	Milk	0.18	0.00
580	Medicated ointment	2.8	1.6
510	Gasoline	0.7	0.0
511	Gasoline	0.7	0.0
512	Gasoline	0.7	0.03
514	Gasoline	0.4	0.01

[a] Samples of atmospheric dust were collected and their weights determined by attaching a dried and tared piece (50 sq. cm.) of specially tested filter cloth to an ordinary domestic air filter and reweighing after exposure and a second drying. Filter and contents were consumed in the analysis.

[b] Samples of vacuum cleaner dust were collected by the ordinary household vacuum cleaner, put through an 80-mesh sieve, and the fines taken for analysis.

[c] In each case the entire cigarette was taken for analysis.

It has been found advisable to use the smallest crucible that will conveniently hold the samples, and to place it in the bomb in such a position that the flame does not come in contact with the walls of the apparatus. The sudden cooling of the flame by contact with the metal surfaces may result in the deposition of tar. Where the material under examination, such as tobacco, manifests a tendency to form tars, a pressure of 30 atmospheres of oxygen should be used in the combustion.

While the Gutzeit zinc-acid evolution (*18*) was employed for the ultimate determination of the arsenic, the method here described for preparation of the sample may be combined with any other methods of determination, as with the Marsh-Berzelius generator or with certain electrolytic modifications of the Marsh or Gutzeit method as recommended by Thorpe (*17*) and Lawson and Scott (*9*). But where the electrolytic evolution of the arsine involves the use of porous cells, the method cannot be considered reliable because of objections taken by Fink (*4*), which are based on possible retention of arsenic by the porous cell.

A predetermined constant strength of the acid solutions and combined washings has been found to provide a uniformity of action in the Gutzeit generator which greatly facilitates accurate quantitative estimations in comparison with a standard scale covering a range of low values, and it is desirable to select a suitable aliquot from the combined washings to fall within the optimum range of from 0.5 to 10.0 micrograms.

Where too dense an ammonium chloride cloud is formed, difficulty is experienced in its complete absorption by the washing train, *C*, *D*, *E*. It has been demonstrated, however, that a complete absorption of the ammonium chloride is not essential to the recovery of the arsenical smoke, probably because the particles of arsenious oxide act as nuclei in the cloud formation and are washed out in its coarser particles. Control of the cloud density is, however, desirable, and is effected by adjusting the concentration of the acid in the nebulizer and more particularly by adjusting the surface area of ammonium hydroxide in reservoir **15**, by rotation of arm 13 in stopper 12, and by application of gentle heat to this reservoir.

Conclusions

In the opinion of the authors the disparity in the results shown in Table II, especially with those samples where the arsenic present was presumably in organic linkage, is attributable to loss by volatilization in the acid-digestion treatment. Should the arsenical organic be resistant to oxidation by the mixed acids, or, should the arsenic linkage be of a fugacious type in minute concentration, even an almost inappreciable vapor pressure at the temperature of boiling acid would account for a considerable loss of arsenic due to the relatively large amount of acid boiled off during the digestion. Experimental support for this opinion was given by an apparent decrease in the arsenical content of certain specimens either during desiccation at relatively high temperatures or on long standing at room temperature.

Negative results have repeatedly been obtained throughout the entire series of experiments, and with other samples the arsenical content has frequently been as low as 0.2 p. p. m., conclusively demonstrating that the large disparity in results is not due to contamination by the equipment or the reagents employed.

Summary

The method which has been described for the destruction of organic matter in preparation for the determination of arsenic prevents the loss of arsenic during combustion and is believed effectually to minimize losses in the process of extracting the combustion products. It is particularly applicable to organic substances and to the detection of minute concentrations of arsenic which may be inherent in or adsorbed to such substances.

The advantages claimed for the method are reliability, simplicity, and speed.

Insurance is provided against losses of organically linked arsenic which may be volatilized by the older methods. Because the process of oxidation is practically instantaneous and within an air-tight vessel and the extractions are carried on within closed vessels, there is no exposure to possible contamination of the sample or reagents by arsenical dust as with oxidations involving lengthy digestions, filtrations, and adsorptions. Simplicity is attained through the use of fewer and smaller quantities of reagents in the oxidation process and the avoidance of acid fumes requiring a hood. The actual time required for preparing samples for arsenic determination is from 15 to 25 minutes, in addition to whatever time may be necessary for dehydration, as against the many hours which are required for the proper performance of an acid-digestion process.

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Sulfur Determination in Sulfite Waste Liquor and Organic Compounds

Potassium Permanganate Method

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THE usual determination of total sulfur in a sample resolves itself into two parts: oxidation of sulfur to sulfate, and determination of the sulfate. For the second part there are a standard method of precipitation with barium chloride and several volumetric methods, but the first step has always presented difficulties to the analytical chemist.

Benson and Benson[1] used five different methods (Schreiber's, Schorger's, fuming nitric acid and potassium chlorate, bromine, and the U. S. Forest Products Laboratory method) for determination of total sulfur content of sulfite liquor, but report considerable difficulty in obtaining check results. The authors had a similar experience with the above methods as well as with the Eschka method and obtained consistently good results only with Parr's sodium peroxide bomb method. Since the bomb is not always available, the following method, which can be used in any modestly equipped laboratory, was developed.

Method

A sample containing enough sulfur to give a barium sulfate precipitate of about 0.15 gram is placed in a porcelain crucible of 25-ml. capacity or larger, 0.5 ml. of concentrated sodium hydroxide solution and 5 ml. of saturated potassium permanganate solution (about 1 gram of potassium permanganate) are added, and the contents of the crucible thoroughly mixed with a little stirring rod. The rod is then removed, care being taken to wash off the adhering mixture into the crucible. After evaporation to dryness on a water bath or in a drying oven the crucible is ignited for half an hour in a muffle furnace or on a Meeker burner at approximately 500° C. A thorough ignition is essential; otherwise low results were invariably obtained. The cooled melt is moistened with a little dilute permanganate solution to oxidize any sulfides which may have formed, and hydrochloric acid is then carefully added, care being taken to prevent loss by effervescence. After evolution of the carbon dioxide has ceased, more hydrochloric acid (total of about 5 ml. of 12 *N* acid or an equivalent amount of dilute acid) is added and the crucible warmed over a steam bath until all manganese dioxide has been converted into soluble manganous chloride. Hot water is then added and the contents of the crucible are filtered through a rapid filter into the precipitating beaker. (Alkali permanganate attacks porcelain crucibles; the amount of silica extracted increases with use of the crucible. On the average, porcelain crucibles can be used only six to eight times, after which results become irregular.) Washing the crucible and the filter is continued until from 200 to 300 ml. of hot water have been used. From this point on analysis proceeds in the usual way: dilution to 400 ml., adjusting the acidity, precipitation with barium chloride, digestion, filtration, ignition, and weighing.

[1] Benson, H. K., and Benson, W. R., Ind. Eng. Chem., Anal. Ed., 4, 220 (1932).

The permanganate method here described has been successfully used by the authors in determination of total sulfur in sulfite waste liquor for a considerable length of time, checks within 0.1 per cent being common, but, as shown by Table II, the method can be used for determination of sulfur in other organic compounds, regardless of its state of oxidation or chemical bonds.

Table I. Sulfur Content of Sulfite Waste Liquor

Sulfite Liquor Sample	By Permanganate Method	By Parr's Bomb Method
	Mg./ml.	*Mg./ml.*
1	8.57	..
	8.57	..
2	8.83	..
	8.80	..
	8.77	..
3	8.45	8.27
	8.47	8.32
	8.50	8.37
	8.22	..

Table II. Determination of Sulfur in Pure Organic Compounds

Compound	Theoretical Percentage of Sulfur	By Permanganate Method: Weight of sample	By Permanganate Method: Sulfur	By Parr's Bomb Method: Weight of sample	By Parr's Bomb Method: Sulfur
		Gram	%	*Gram*	%
Sulfanilic acid	18.52	0.1849	18.36	....	...
		0.1908	18.48	....	...
		0.2300	18.45	....	...
Trional	26.47	0.0809	26.35	0.0855	26.25
		0.0995	26.30	0.0898	26.24
		....	...	0.1702	26.20
Thiourea	42.13	0.0616	42.02	....	...
		0.0740	41.94	....	...
		0.0700	42.13	....	...

Table III. Effect of Presence of Manganous Chloride on Barium Sulfate Precipitate

Manganous chloride present ($KMnO_4$ equivalent)	None	1 gram	2 grams
	Gram	*Gram*	*Gram*
Barium sulfate precipitated	0.2010	0.2009	0.2021
	0.2015	0.2017	0.2018
	0.2016	0.2014	0.2020
Av.	0.2014	0.2014	0.2020

Discussion

Table I gives a typical set of checks obtained in sulfur determination of three samples of sulfite waste liquor by the alkali permangante method and a comparison of one set with results obtained by Parr's method. In the determination by the permanganate method, 2-ml. samples of the liquor were used, while in the determination by bomb method 25 ml. of the liquor were neutralized and evaporated to dryness,

and the weight of the solids was determined. The solids were then ground and samples weighed out, the sulfur content was determined, and the results obtained were recalculated on the volume basis. The slight difference in the results may be due to the difference in methods of taking samples.

Table II gives results of sulfur determination on pure sulfur-containing substances. The values obtained are in sufficiently close agreement with the theoretical.

Table III gives results of precipitating sulfates from 10 ml. of known sodium sulfate solution in the presence of various amounts of manganous chloride. It shows that an amount equivalent to 1 gram of potassium permanganate (the amount used in the authors' procedure) has no effect, and twice that amount gives a variation of only 6 parts in 2000.

The chief advantages of the permanganate method are: It is simple; no special apparatus is required; there is nothing to regulate or watch; and only small quantities of very common inexpensive reagents are used. The method can be used for oxidation of sulfur compounds in water solutions (like sulfite waste liquor) without preliminary evaporation to dryness. The oxidation is rapid and complete in cases tried and the results agree closely with either those obtained by the peroxide bomb or with the theoretical percentages as shown by Tables I and II. Compounds which will float on the surface of the alkaline permanganate solution cannot be completely oxidized, owing to loss by evaporation or sublimation.

The two filtrations in the procedure are time-consuming. However, if crucibles were made of a material which is resistant to both alkali permanganate and hydrochloric acid, such as acid-resistant alloys, the first filtration would be eliminated and the time necessary for the determination cut to two-thirds of that required at present. The authors did not have such crucibles at hand.

Acknowledgment

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Colorimetric Determination of Iodine by the Starch-Iodine Reaction

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The use of the starch-iodine reaction for the quantitative determination of iodine has been considered by von Fellenberg (*3*), Remington et al. (*7*), and others to be unsatisfactory, and the method has seldom been used, although Turner (*10*) employs it over a limited concentration range. Examination of the literature of starch-iodine suggests a number of possible sources of error in the use of its formation for the determination of iodine. While Dhar (*2*) considers that a true but unstable compound between starch and iodine is formed, most authors agree that the union of starch and iodine is by adsorption. Gorbatscheff and Winogradowa (*5*) claim that molecular iodine is adsorbed. Angelescu and Mirescu (*1*), Firth and Watson (*4*), and others consider that the blue color is due to the adsorption of potassium triiodide by starch, while Gramenitski (*6*) and Staiger (*8*) present evidence to show that hydriodic acid is the substance adsorbed. It was early pointed out by Treadwell (*9*) that the starch-iodine compound is readily dissociated at low concentrations.

The present investigation was undertaken in order to develop a rapid method of determining iodine in the presence of 10 per cent of potassium iodide. A study was made of the influence of potassium iodide, acids, and salts on the intensity of the starch-iodine color, and the degree of dissociation of the compound was estimated under a number of different conditions.

Method. The method has been described in detail in a previous publication (*11*). A stock solution of approximately 0.025 per cent iodine in approximately 0.2 per cent potassium iodide was prepared and standardized by titration against sodium thiosulfate. Portions of this were then diluted with starch and potassium iodide solution in 10- or 25-cc. volumetric flasks as required, and read in the colorimeter. For part of the work a solution of iodine in 25 per cent ethyl alcohol instead of 0.2 per cent potassium iodide was used. The stock starch solution was prepared by making a paste of 2 grams of soluble starch with 30 cc. of cold water, adding this slowly to 70 cc. of boiling water, and boiling for 5 minutes. The solution was made fresh every 3 or 4 days. The colorimeter used was a Klett instrument having cups and plungers with black walls, and substage illumination through blue glass.

Results

The effect of potassium iodide on the intensity of the starch-iodine color was studied by adding small quantities of potassium iodide to solutions containing 2.5 per cent alcohol, 0.5 per cent starch, and 1.8 and 5.0 mg. of iodine per 100 cc. It was found that the intensity of color increased rapidly with increasing potassium iodide concentration until the normality ratio of potassium iodide to iodine reached 0.35. This ratio must therefore be equaled or exceeded whenever iodine is to be determined by the starch-iodine reaction. Further additions of potassium iodide caused a slight increase in color intensity until at 1 per cent concentration it became purplish. The color became progressively redder and fainter with increasing concentration of potassium iodide beyond this point. In general it was found that differences in concentration insufficient to change the tint of the starch-iodine color caused no significant change in the intensity of the color, and could be disregarded in analytical work. It is probable that addition of small quantities of potassium iodide to the alcoholic starch-iodine solution increases the intensity of color through the formation of potassium triiodide, which gives the characteristic deep blue compound with starch. Further additions of potassium iodide after all the iodine has been converted to potassium triiodide may then change the tint and intensity of the color by changing the colloidal state of the compound.

Starch-iodine solutions containing sufficient potassium iodide to be definitely reddish do not obey Beer's law with some types of illumination. The deviation is small when the blue filter at present provided with the Klett biocolorimeter is used. In the preparation of the correction curves (Figure 1) the colorimeter plunger was set always at the same depth in the standard solution. The same standard setting was then used for making readings on unknown solutions which were

to be corrected by means of the curve, so that error due to depth effect was avoided.

The effect of concentration of starch on the intensity of color developed in solutions containing 2.4 mg. of iodine plus 20 mg. of potassium iodide per 100 cc. and 5.1 mg. of iodine plus 40 mg. of potassium iodide per 100 cc. was studied. The maximum color was developed when about 40 mg. of starch per mg. of iodine were present. All the correction curves given were obtained with solutions containing 0.5 per cent starch, so that excess was always present beyond the amount necessary to combine with all the iodine. It was found that aging of the starch solution used had no effect on the starch-iodine color so long as the starch remained only faintly opalescent.

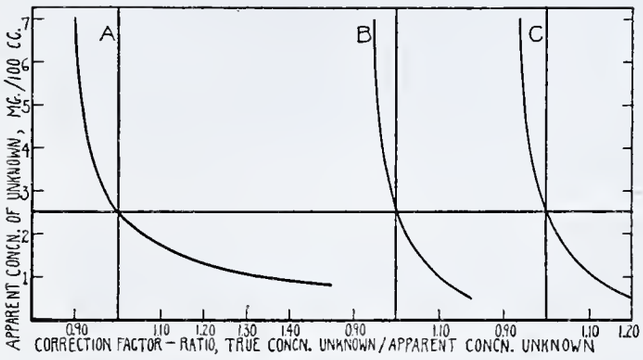

Figure 1. Correction Curves

The dissociation of the starch-iodine compound was found to be the most important source of error in the analytical method. In order to study this, iodine solutions of different concentrations were made up in 0.5 per cent starch with or without potassium iodide in known concentrations. These solutions were then read against a standard containing 2.5 mg. of iodine per 100 cc. The results of this work are given in the form of correction curves in which the apparent concentration of the unknown is plotted against the correction factor to be applied. This method of plotting shows the effect of dissociation of the starch-iodine compound very clearly, but in actual practice it is more convenient to use correction curves in which the apparent concentration of the unknown is plotted against the absolute correction in mg. per 100 cc.

Curve A, Figure 1, shows the correction factors for iodine solutions in 2.5 per cent alcohol and 0.5 per cent starch, when read against a standard containing 2.5 per cent alcohol, 0.5 per cent starch, and 2.5 mg. of iodine per 100 cc. Fifty determinations were made, with an average error of ±4 per cent. When the unknown is more concentrated than the standard its apparent concentration is too large, and when less concentrated its apparent concentration is too small. This is evidently due to the dissociation of the starch-iodine compound. From the fact that the correction factor becomes nearly constant when the apparent concentration of the unknown is 5 mg. per 100 cc. or more, it seems likely that the dissociation of the compound is small above this concentration. On the other hand, the dissociation is so great in dilute solution that the method is of little use when the iodine concentration is below 1.5 mg. per 100 cc. Furthermore, the intensity of the starch-iodine color in the absence of potassium iodide is so readily affected by contamination with electrolytes that the method is reliable only under very special conditions.

Curve B, Figure 1, shows the corrections for iodine solutions containing 0.5 per cent starch and about 8 mg. of potassium iodide per mg. of iodine, when read against a standard containing 2.5 mg. of iodine and 20 mg. of potassium iodide per 100 cc., and 0.5 per cent starch. Fifty-five determinations were made with an average error of ±2 per cent. The dissociation in this system is much less than in system A, and the method may be used for iodine concentrations down to 0.5 mg. per 100 cc.

Curve C, Figure 1, shows the corrections for iodine solutions in 10 per cent potassium iodide and 0.5 per cent starch, read against a standard containing 2.5 mg. of potassium iodide per 100 cc., 10 per cent potassium iodide and 0.5 per cent starch. Eighty determinations were made, with an average error of ±2.5 per cent. The curve is similar to B, but the corrections are a little larger. This does not necessarily mean that the dissociation of the starch-iodine compound is greater in 10 per cent potassium iodide, but is probably due to the optical peculiarities of the solution. A correction curve was also obtained for solutions in 10 per cent potassium iodide read against a standard containing 1.0 mg. of iodine per 100 cc. When allowance was made for the greater dissociation of the more dilute standard, this curve was practically identical with C.

After correction factors for dissociation had been obtained it was possible to study the effect of acids and salts. This was done for solutions containing 8 mg. of potassium iodide per mg. of iodine, and for solutions in 10 per cent potassium iodide. Unknowns containing 1.1, 2.3, and 4.6 mg. of iodine per 100 cc. and 0.5 per cent starch were made up in 0.1 *N* solutions of different acids and salts and read against a standard containing 2.5 mg. of iodine per 100 cc., 0.5 per cent starch, and no added acid or salt. The apparent concentration of the unknown was then compared with that of iodine solutions of the same concentration prepared without acids or salts, as shown in the correction curves. The results are shown in Table I, each value being the average of 7 determinations.

Table I. Error Introduced by Contaminant

	Solutions Containing 8 mg. of KI per mg. of I			Solutions in 10 per cent KI		
	True iodine concentration, mg. per 100 cc.			True iodine concentration, mg. per 100 cc.		
	1.1	2.3	4.6	1.1	2.3	4.6
Contaminant 0.1 *N*	*Mg./100 cc.*	*Mg./100 cc.*	*Mg./100 cc.*	*Mg./100 cc.*	*Mg./100 cc.*	*Mg./100 cc.*
Na_2SO_4	+0.11	+0.17	+0.17	−0.04	−0.02	+0.02
$NaNO_3$	+0.11	+0.15	+0.19	−0.01	−0.01	0.00
NaCl	+0.10	+0.15	+0.19	−0.02	−0.05	+0.06
$CaCl_2$	+0.07	+0.19	+0.26	−0.02	0.00	0.00
H_2SO_4[a]	+0.11	+0.12	+0.12	+0.12	+0.12	+0.12
HNO_3[a]	+0.12	+0.15	+0.14	+0.11	+0.16	+0.25

[a] Acid concentration in solutions in 10 per cent potassium iodide, 0.05 *N*.

The presence of salts in 0.1 *N* concentration causes appreciable errors in the determination of iodine in solutions containing minimal quantities of potassium iodide, but not in solutions containing 10 per cent potassium iodide. For the former solutions the effect of sulfuric and nitric acids is the same as that of sodium sulfate and sodium nitrate, from which it appears that the adsorption of hydriodic acid by starch is not an important factor in the production of the starch-iodine color. The effect of acids on solutions in 10 per cent potassium iodide is probably due to an increase in the actual concentration of iodine through decomposition of potassium iodide. This takes place rapidly in concentrated potassium iodide solutions, and may have been appreciable in the 2 or 3 minutes which elapsed between addition of acid to the solutions and making the readings.

Investigation of solutions containing 0.1 *N* disodium phosphate or sodium hydroxide in low concentration showed that large errors were introduced as soon as the pH of the solution rose above 7.

Summary

The most important source of error in the colorimetric determination of iodine by means of the starch-iodine reaction was found to be the dissociation of the starch-iodine compound. Correction factors are given for the determination of iodine in the concentration range from 0.5 to 7.0 mg. of iodine per 100 cc. The effect of the concentration of starch and potassium iodide, and of the presence of contaminating acids and salts has also been investigated.

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Determination of Lead Soap in Oils and Greases

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It is frequently necessary during the examination of greases, car oils, extreme pressure lubricants, etc., to determine the amount of lead soap present. Various methods have been published for this determination but most of them are inaccurate, difficult, or tedious. The methods generally involve the determination of the combined lead present, from which, by suitable factors, the percentage of lead soap is calculated. The more common methods for the determination of the combined lead are the following:

1. The direct ignition of a weighed portion of sample, the ash being recorded as lead oxide.

This procedure leads to inaccurate results because the ash is practically never pure lead oxide, but contains metallic lead and usually iron oxide.

2. The direct ignition of a weighed portion of sample, followed by digestion with sulfuric acid to convert all the lead present to lead sulfate, which in turn is dissolved in ammonium acetate and subsequently precipitated and determined as the chromate.

This procedure, while sound in principle, is lengthy and offers difficulties in manipulation.

3. The sample is digested with concentrated sulfuric acid followed by ignition of the mass, leaving the lead as sulfate. From this point on, the procedure is the same as the second method.

This method is even more difficult than the second, the oil and sulfuric acid frothing to such an extent as to cause losses.

The procedure which has been developed in the author's laboratory has proved universally satisfactory, even in the hands of comparatively inexperienced operators. It is based on the fact that the sample being analyzed is soluble in a homogeneous mixture of pure benzene and glacial acetic acid, and upon being refluxed the lead compounds are converted to acetate which can subsequently be precipitated as lead chromate. Incidentally, this procedure, if slightly modified, distinguishes between the organic and inorganic lead, the latter resulting either from excess of litharge used in the saponification process or consisting of lead sulfide formed by the interaction of litharge with the sulfur compounds of the mineral oils.

Procedure

The reagents required are a 10 per cent potassium chromate solution, a mixture of glacial acetic acid and pure benzene (1 to 2 by volume), and pure benzene.

Two to ten grams of sample, depending upon the concentration of lead soap, are weighed into a suitable Erlenmeyer flask, 45 cc. of the glacial acetic acid–benzene mixture are added, and the mass is boiled actively under a reflux condenser for 1 hour. It is allowed to cool, and is then transferred to a globe-shaped separatory funnel, the flask being rinsed with two successive 10-cc. portions of the glacial acetic acid–benzene mixture.

To the separatory funnel are added 50 cc. of distilled water, the contents are gently shaken and allowed to settle, and the aqueous layer is withdrawn into another separatory funnel. Experience has shown that when decomposition has been completed the layers separate rather sharply. Emulsions usually indicate incomplete decomposition.

The benzene layer is washed with 50-cc. portions of distilled water until the aqueous extract is free of acetic acid. Combined aqueous washings are then filtered through wet paper to remove entrained oil, and the lead in the filtrate is precipitated as chromate by the addition of an excess of 10 per cent potassium chromate solution.

When the precipitate is thoroughly settled and the upper layer is perfectly clear, it is filtered on a Gooch, washed thoroughly with hot water, dried at 105° C., and weighed as lead chromate. By a suitable factor the lead chromate is converted to the particular lead soap involved—for example, lead chromate multiplied by 2.381 gives lead oleate; lead chromate multiplied by 2.949 gives lead naphthenate, of a naphthenic acid whose molecular weight is 374.

Tables I and II indicate the reproducibility of results by the different methods in the hands of a competent chemist who had not used any of these methods before. It is apparent that the proposed method was the only one which consistently gave reproducible and accurate results. The solvent used for the solution samples was a pale mineral lubricating oil.

Table I. Determination of Lead Soap as Oleate

Sample	Method 1		Method 2		Method 3		Proposed Method	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
	%	%	%	%	%	%	%	%
Lead oleate, comm.	102.1	97.0	94.5	91.6	96.6	53.3	96.5	96.4
3 per cent lead oleate, solution	4.3	3.1	1.8	0.7	..[a]	..[a]	2.79	2.82
10 per cent lead oleate, solution	11.4	11.0	8.8	5.3	..[a]	..[a]	9.73	9.59

[a] Lost by violent spattering or uncontrollable frothing.

Table II. Determination of Lead Soap as Naphthenate

Sample	Method 1		Method 2		Method 3		Proposed Method	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
	%	%	%	%	%	%	%	%
Lead naphthenate, comm.	84.6	84.6	80.1	58.0	86.6	82.1	86.4	86.2
3 per cent lead naphthenate, solution	2.57	2.67	2.25	1.93	1.33	1.20	2.53	2.53
10 per cent lead naphthenate, solution	8.3	9.1	8.1	7.3	8.60	8.37	8.56	8.56

The naphthenic acid component of the lead naphthenate used in these tests had a molecular weight of 374.

When it is desired to distinguish between the organically combined lead present as lead soap and the inorganic lead compounds, the procedure should be modified: The weighed sample is first refluxed with benzene, then filtered as hot as possible through the Gooch crucible, and to the filtrate is then added the required amount of glacial acetic acid to give the proportion indicated above; the rest of the procedure for organically combined lead is identical with that outlined. Experience with a great many commercial lead soap lubricants has shown very few lead soaps, basic or otherwise, which are not soluble in boiling benzene. The inorganic lead compounds which remain insoluble in the benzene can be digested with nitric acid and the lead determination carried out in the usual manner.

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The Microanalysis of Gases

III. Hydrogen, Carbon Monoxide, Hydrogen Chloride, and Ammonia

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In THIS article the methods of microanalysis of gases which were described earlier (*1*, *2*) are extended to include a new method for the determination of hydrogen and carbon monoxide, and to include hydrogen chloride and ammonia as gases which may be determined by known procedures.

Additions to Apparatus

In applying the methods of microanalysis, it has not always been possible to collect the gas directly in the analytical apparatus, and it has therefore been necessary to arrange for the transportation of samples. A circular iron pneumatic trough, 2 cm. in diameter and 1 cm. in depth, which can be lowered into the mercury reservoir of the analytical apparatus (*2*, Figure 1), is welded to an adjustable iron arm of a small ring stand. A second adjustable arm carries a steel spring clamp into which the gas holders can be slipped by a horizontal movement. This device makes it possible to take a small sample of gas to or from the main apparatus without danger of loss or contamination.

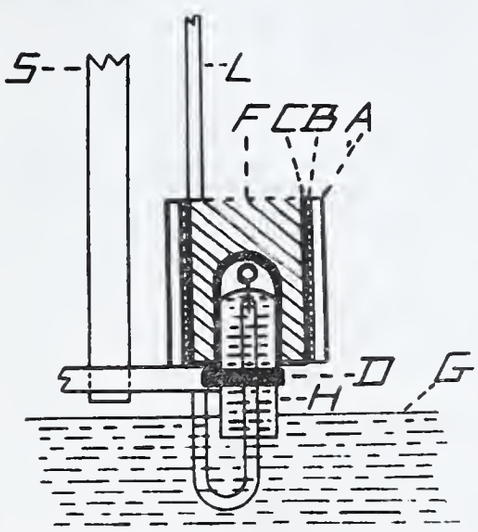

Figure 1. Diagram of Gas Heater

Recently, Pierce, Friedenwald, and Freeman (*8*) have described an alternative means of transferring gas samples, which in certain studies may be more desirable than the one herein described, although it is more liable to introduce impurities into the gas. Swearingen, Gerbes, and Ellis (*9*) describe a similar apparatus.

In developing the method for the analysis of hydrogen, it was found necessary to elevate and control, within limits, the temperature of the gas sample. The method adopted does not give the true temperature of the reaction system but does give an upper limit above which the temperature cannot go. There are other more exact means of temperature control, but it has been the desire of the authors to attain simplicity of method and construction whenever this could be done without the sacrifice of results. The heater which has been devised is shown in cross section in Figure 1.

The gas holder, *H*, is shown in its normal position over the mercury reservoir of the microanalytical apparatus. *C* is a copper vessel. Projecting up in the center of *C* is a cavity which is shaped to fit snugly around the gas holder. The upper part of *C* is hollowed out forming the space, *F*, which is approximately 1.5 cm. in diameter and 2.5 cm. in depth. This vessel may be machined directly from a solid rod, or made in pieces and then put together by means of silver solder. Around *C* is wrapped a thin layer of mica, then the electrical heating coil, *B*, and finally asbestos sheet *A*. In *F* are placed about 2.5 cc. of some relatively stable solid substance which has a definite, known melting point.

In operation, the gas sample is introduced in the usual way and the absorbent placed in position. The heater is then slipped over the gas holder and the electrical current applied. When most, but not all, of the substance in *F* has melted the heating is discontinued. Since the thermal conductivity of the mercury reduces the temperature of the gas much below that attained in the heater, a solid substance has to be chosen which has a melting point somewhat higher than that desired in the gaseous system. Potassium dichromate and lead were both found to be satisfactory in the analyses which are described.

Specific Methods of Analysis

Hydrogen. In certain photochemical studies it has become very important to determine the presence or absence of small amounts of hydrogen in the products of photolysis. The explosion method (*1*) is only moderately accurate at best and is valueless for the determination of small percentages of hydrogen in the presence of several saturated hydrocarbons.

The problem of selectively absorbing this gas in the presence of other combustible gases has been met in macroanalysis by oxidation with copper oxide in a temperature-controlled dynamic system (*3*, *5*), but application of this method to the authors' problem was not successful. Experiments were made with mixtures of hydrogen and nitrogen of known percentage composition. A bead of cupric oxide was prepared by fusion in a platinum loop with the aid of a blast lamp. The gas sample was heated to a temperature somewhat below the melting point of potassium dichromate by means of the electric heater described above. After sufficient time had been allowed for the oxidation of the hydrogen, the copper oxide and heater were removed and phosphorus pentoxide was introduced to take up the water vapor formed in the reaction. Although considerable oxidation did occur, it was found impossible to remove all the hydrogen in this way. In this static system, it is possible that an equilibrium condition was reached before oxidation was complete. This idea is substantiated by the fact that a second bead of the oxide placed in the same sample removed more, but not all, of the remaining hydrogen.

Assuming that the foregoing explanation is correct, it was reasoned that if the moisture produced could be removed from the gaseous phase as it was formed, complete oxidation of the hydrogen would occur. This involved the simultaneous introduction of the oxidizing agent and a drying agent into the gas sample. A bead made by fusing together cupric oxide and potassium hydroxide accomplishes this purpose and can be used for the rapid and complete absorption of hydrogen.

The reagent is prepared by first fusing the oxide in the platinum loop and then touching the molten mass to an approximately equal amount of the solid hydroxide. The two substances coalesce and, after cooling, a smooth, dark blue bead results. By heating the gas sample in the presence of this solid, hydrogen is readily oxidized and the water formed in the reaction is absorbed at the same time. The decrease in volume represents directly the amount of hydrogen in the sample. Absorption is very rapid and the time required for the complete analysis does not exceed 15 minutes.

Known mixtures of hydrogen with nitrogen, butane, and methane have been analyzed with the success indicated in Table I. Lead was the substance used in the heater. Potassium dichromate is equally satisfactory as far as the separation of hydrogen from other gases is concerned, but because of its high melting point (398° C.) there is danger of vaporizing the mercury and losing the sample of gas. It has been found by one of the authors, while working at relatively high altitudes, that under these conditions lead and not potassium dichromate must be used because of this danger.

Table I. Results of Analyses of Hydrogen and Methane Mixtures

Determination	Volume of Sample	Hydrogen Theoretical	Hydrogen Determined	Difference
	Cu. mm.	%	%	%
1	86.51	46.49	46.30	−0.19
2	97.43	38.11	38.00	−0.11
3	83.35	52.00	52.18	+0.18
4	87.98	47.38	47.17	−0.21
5	91.45	44.25	44.20	−0.05
		Average difference		0.15
		Average deviation from mean		0.11

Carbon Monoxide. Carbon monoxide may be selectively oxidized in the presence of methane, and other members of its series, by the same reagent and method as hydrogen and with approximately the same degree of accuracy. Lead was used for temperature control in obtaining the values in Table II.

By lowering the temperature of the reaction system, attempts were made to remove carbon monoxide by this cupric oxide–potassium hydroxide reagent in the presence of hydrogen. These experiments, however, were not successful. Temperatures sufficiently low to leave the hydrogen unoxidized gave incomplete removal of the carbon monoxide.

Table II. Results of Analyses of Carbon Monoxide and Methane Mixtures

Determination	Volume of Sample	Carbon Monoxide Theoretical	Carbon Monoxide Determined	Difference
	Cu. mm.	%	%	%
1	88.37	50.81	50.81	0.00
2	86.40	47.77	47.59	−0.18
3	87.32	49.05	49.20	+0.15
4	89.41	42.64	42.64	0.00
5	92.34	44.78	44.68	−0.10
		Average difference		0.09
		Average deviation from mean		0.09

Hydrogen Chloride. Gaseous hydrogen chloride may be absorbed by the method described for carbon dioxide (*1*). An alternative method is to use a concentrated potassium hydroxide solution in a sintered glass bead. The procedure in this case is similar to that which is employed for the determination of ethylene (*2*), except that the concentrated alkali is used instead of sulfuric acid. The water vapor pressure over this absorbent is small and may be neglected in the analysis.

In both methods the absorption process is very rapid, 2 minutes being ample to allow in any case for complete removal of the hydrogen chloride. Because it is slightly more convenient to use, the authors prefer the second method and the results given in Table III were obtained in this way. The samples were mixtures of hydrogen chloride with dry, carbon dioxide–free air.

Table III. Results of Analyses for Hydrogen Chloride

Determination	Volume of Sample	Hydrogen Chloride Theoretical	Hydrogen Chloride Determined	Difference
	Cu. mm.	%	%	%
1	154.38	50.81	50.91	+0.10
2	148.79	49.43	49.47	+0.04
3	148.30	48.81	48.81	0.00
4	145.71	48.22	48.26	+0.04
5	138.92	45.39	45.45	+0.06
		Average difference		0.05
		Average deviation from mean		0.03

Ammonia. Ammonia has been absorbed by the use of a moistened phosphorus pentoxide bead prepared as previously described (*1*) and also by means of concentrated sulfuric acid in sintered glass. There is little choice to be made between these methods. As far as absorption of ammonia is concerned, both reagents will give constant results very rapidly. However, in analyzing prepared samples of ammonia mixed with nitrogen or hydrogen, consistently high percentage values of ammonia were obtained. Since the nitrogen or hydrogen was always treated with phosphorus pentoxide or sulfuric acid before it was mixed with ammonia, these abnormal values were not due to impurities of ammonia or similar gases.

In Table IV are given consecutive results of analyses of mixtures of ammonia and hydrogen, using phosphorus pentoxide as the absorbent. Although the results, which are typical of over fifty separate analyses, are sufficiently accurate for most purposes, they are not as good as results obtained for other gases.

Table IV. Results of Analyses for Ammonia

Determination	Volume of Sample	Ammonia Theoretical	Ammonia Determined	Difference
	Cu. mm.	%	%	%
1	95.00	48.00	48.40	+0.40
2	104.20	46.26	46.42	+0.16
3	97.20	49.59	49.78	+0.19
4	108.90	46.37	46.57	+0.20
5	104.60	49.04	49.34	+0.30
		Average difference		0.25
		Average deviation from the mean		0.08

Discussion and Summary

The apparatus used for the studies herein described was the same as that described before (*2*), except for the additions indicated. Pierce, Friedenwald, and Freeman (*8*) have suggested the use of an ivory tip to insure bringing back the mercury in the reservoir to the same level each time before reading the gas volume in the buret. Swearingen, Gerbes, and Ellis describe a similar gas analysis apparatus in which a horizontal buret is used (*9*).

Although the percentage composition of small gas samples can be determined to the degree of accuracy indicated in the several methods outlined, the absolute volume of samples cannot be ascertained with equal precision by capillary burets. In order to test this point, several relatively large volumes of air, measured by weighing the same volume of mercury, were measured in steps using the microburet. The buret readings gave an average of 1.8 per cent larger total volume than that obtained by weighing the mercury. Using the data given in International Critical Tables (*4*) for the surface tension of mercury and for the contact angle of mercury and glass, corrected volumes were obtained which were 1.1 per cent smaller than those obtained by weighing mercury. No doubt this correction is too great, because under working laboratory conditions where the walls of the buret may not be perfectly clean, the values for surface tension and contact angle must be somewhat smaller than those given in the literature. Since we cannot know these values, because of constantly changing conditions of cleanliness, adsorbed gases, etc., the absolute volume of small gas samples cannot be determined with great accuracy. Using the authors' data and buret, which has a capillary diameter of 0.52 mm., a negative correction of 1.8 per cent would give the absolute volume of gas to within ±0.5 per cent.

Burets having diameters up to 0.7 mm. are being used by the authors. In operating all of these, the effect of the surface tension of mercury is pronounced. Capillaries much larger than these would require unduly large samples in order to obtain the highest percentage accuracy in analyses.

The consistently high values obtained for ammonia may be due to the low surface tension of mercury when ammonia is in contact with it (*4*). It has been suggested (*9*) that solid

potassium bisulfate may be used to absorb ammonia, but no quantitative results are available.

In using sulfuric acid in sintered glass beads, it has been stated by others using this method that the acid may spread over the surface of the mercury. The authors, using sintered beads made from 100- to 150-mesh soft glass and following the procedure previously outlined (*2*), have not experienced this difficulty. However, if too much acid is left on the bead and spreads over the mercury, it can be removed by the use of a follow-up bead of potassium hydroxide.

Table V. Summary of Gases Analyzed and Reagents Used

Gases	Reagents
Water vapor	Potassium hydroxide or phosphorus pentoxide (*1*)
Carbon dioxide, hydrogen chloride, and other acid-producing gases	Potassium hydroxide (*1*)
Acetaldehyde, and vapors of similar compounds	Potassium hydroxide (*6*)
Oxygen	Phosphorus (*1*)
Ammonia and other base-producing gases	Phosphorus pentoxide, or concentrated sulfuric acid in sintered glass
Acetylene	Cuprous chloride and potassium hydroxide (*2*)
Ethylene and other unsaturated hydrocarbons	Concentrated sulfuric acid (fuming, for ethylene) (*2*)
Carbon monoxide	Silver oxide (*2*), cupric oxide and potassium hydroxide, or explosion (*1*)
Hydrogen	Cupric oxide and potassium hydroxide, or explosion (*1*)
Methane and ethane, or any two readily combustible gases	Explosion (*1*)
Nitrogen and other inert gases	By difference

The dark blue bead for the oxidation of hydrogen and carbon monoxide probably consists in part of a solid solution of cupric oxide in potassium hydroxide (*7*). The color is a good indication of the effectiveness of the bead as an absorbing agent. Care should be taken not to use a large excess of potassium hydroxide and this hydroxide should be relatively pure. The presence of an appreciable amount of potassium carbonate seems to reduce the reactivity of the absorbent.

It is evident that this cupric oxide–potassium hydroxide reagent cannot be used to effect a separation of carbon monoxide and hydrogen. The silver oxide method does this very well with the limitations previously described (*2*).

The methods for the microanalysis of gases described in this series of articles have been developed to the point where they may be used successfully to determine quantitatively an appreciable number of the more common gases. In Table V may be found summarized the gases which have been studied by the authors in this way, along with the reagents and methods employed. By absorbing the gases in the proper sequence, almost any compatible mixture of these gases may be analyzed. For example, the following nine gases could be systematically separated by removing them in the order named: water, carbon dioxide, ethylene, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen. It should be possible to accomplish this separation, using an original sample of 100 cu. mm., with the same degree of accuracy as by standard macroanalytical methods using an original sample of 100 cc.

Acknowledgment

The authors wish to acknowledge their indebtedness to P. A. Leighton for his kindly interest and many suggestions in regard to this work.

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Anhydrous Sodium Carbonate for Standardization

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Sodium carbonate has been used as a standard for many years in neutralization methods of analysis. Many textbooks quote Lunge (*4*) and require that, in the preparation of sodium carbonate from sodium bicarbonate, the sample should not be heated over 300° C. Some state that sodium carbonate decomposes above this temperature; some, that it becomes hygroscopic. It was the purpose of the authors to investigate thoroughly the whole matter of preparation, as well as the mass of conflicting statements.

Experimental

Reagents. Stock c. p. sodium bicarbonate, such as is available in any laboratory, was used as a starting material for sodium carbonate preparation. In terms of sodium bicarbonate this material analyzed 100.45 per cent.

The hydrochloric acid solution was prepared from redistilled hydrochloric acid and water redistilled from alkaline potassium permanganate solution. The acid was standardized against calcite, benzoic acid, and potassium acid phthalate, making suitable corrections for indicators. The error in standardization was 1 part in 2500.

The sodium hydroxide solution was prepared carbonate-free by the method of Cornog (*1*).

Preparation of Sodium Carbonate. Sodium bicarbonate decomposes to sodium carbonate at any temperature above 102° C. A sample heated at this temperature for one week analyzed 100.20 per cent in terms of sodium carbonate. When heated to higher temperatures a well-stirred sample remained at 140° for some time. Samples heated to 150° C. and cooled at once were found to be completely converted. It is obvious therefore that any sample heated above 150° C. is completely converted, regardless of the length of time of heating.

Table I. Results of Heating Sodium Bicarbonate

Temperature of Conversion	Time of Heating	Per Cent in Terms of Na_2CO_3
° C.	Hours	
102	1 week	100.20
115	1 week	100.04
165	24	100.10
200	24	100.15
260	12	100.07
260	24	100.09
260	48	100.17
300	24	100.09
375	24	100.13
375	48	100.10

It would seem from the analyses in Table I that temperature and time of heating made very little difference. There is no indication of decomposition at temperatures as high as 375° C.

Instability. Instability in the presence of moist air and moist, carbon dioxide–laden air is rather difficult to measure. The results in Table II should be taken only qualitatively. The samples were those of Table I (of 24 hours' heating) and were in all cases exposed for 6 hours.

Table II. Instability of Sodium Carbonate

Temperature of Conversion	Exposure	Na_2CO_3
° C.		%
260	Moisture	98.80
375	Moisture	99.86
260	Carbon dioxide and moisture	78.50
375	Carbon dioxide and moisture	97.85

Table III illustrates the results obtained under the same conditions as in Table II, but using pure sodium carbonate, prepared by washing with ethyl alcohol, recrystallizing, and drying at 110° C.

Table III. Instability of Pure Sodium Carbonate

Exposure	Na_2CO_3
	%
Carbon dioxide and moisture	91.62
Moisture	98.36

It is obvious that both pure and impure sodium carbonate are subject to change on exposure, regardless of the temperature at which they have been heated. No other conclusions should be drawn from Tables II and III.

Impurities. The nature of the impurities causing high results on the samples of sodium carbonate and bicarbonate was not easily discovered. Carbon dioxide analyses were made on several samples but the results could not be made sufficiently precise to warrant any conclusions. It is significant, however, that a sample of sodium carbonate, washed with ethyl alcohol and dried, analyzed, by neutralization methods, 100.00 per cent within experimental error. This would lead one to suspect sodium oxide or hydroxide, since sodium hydroxide is soluble in ethyl alcohol.

Table IV illustrates some results of washing sodium bicarbonate alcohol before conversion to sodium carbonate, and washing sodium carbonate after its preparation. The temperature of preparation of sodium carbonate was 260° C.

Table IV. Results of Washing

	Na_2CO_3	Av.
	%	
Sodium bicarbonate washed before conversion	100.18 100.17	100.17
Above sodium carbonate washed after conversion	100.00 100.05 100.03	100.03
Sodium carbonate prepared directly from C. P. sodium bicarbonate and washed after conversion	100.02 100.04	100.03

It is obvious from Table IV that some sodium oxide or hydroxide is formed in the conversion of sodium bicarbonate to carbonate regardless of temperature, since all previous samples analyzed high. Further evidence that no other decomposition takes place is given by Table V in which samples of the above purified sodium carbonate were heated.

Table V. Results of Heating Purified Sodium Carbonate

Temperature of Heating	Time	Na_2CO_3
° C.	Hours	%
100	24	100.04
375	24	100.05

Vapor Pressure. Johnson (*3*) has found that at 940° C. sodium carbonate exerts a pressure of 5 mm. of mercury and at 1100°, 10 mm. of mercury. Measurements were made in this laboratory at temperatures up to 940° C., using an evacuated system and a calibrated McLeod gage. Precautions were taken by prolonged pumping and heating to drive off all adsorbed gases inside the system before a determination was made. These precautions were the result of the work of Hariba and Baba (*2*) on the vapor pressure of sodium and potassium chloride.

The pumps were sealed from the system and the pressure was checked for 6 hours before heating the sample. Pressures were read at 10° intervals during heating, allowing 20 minutes at constant temperature for each reading. The first observable pressure due to decomposition was shown at 482° C. The average of several trials was 499° C. This eliminates any possibility of decomposition below 450° C., a temperature far above any needed for preparation of sodium carbonate from sodium bicarbonate.

Crystal Structure. It was thought that a change in crystal structure might be responsible for the previously mentioned theories of decomposition. X-ray photographs of samples at 25°, 260°, 300°, and 375° C. were made by the powder method, using a heater to maintain the sample at the above temperatures. In no case was any change in structure found, other than the expected shift of lines due to expansion. The authors were unable to prepare crystals large enough for a complete crystal analysis, but were able to check the petrographic results of Winchell (*5*), who states that sodium carbonate crystals from fusion are biaxial, negative, with $2V = 34° \pm 3°$. The authors, using crystals grown from fused sodium hydroxide, also noted that the crystals appear to have three good cleavages and show marked lamellar twinning. Extinction angles with the cleavage were found varying from zero to 30°. From the above evidence, it appears that anhydrous sodium carbonate may be monoclinic.

Conclusions

Washing so-called C. P. anhydrous sodium carbonate with ethyl alcohol and drying it at 110° C. render it satisfactory as a volumetric standard. Anhydrous sodium carbonate does not decompose below 450°, nor does it change its crystal structure below 375° C. The impurities leading to high results are very probably due to sodium oxide and (or) hydroxide and come from the decomposition of sodium bicarbonate during its conversion to sodium carbonate.

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Precise Method for Determining Ammoniacal Nitrogen in Eggs

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An apparatus which renders possible the precise determination of ammoniacal nitrogen by aëration of alkaline mixtures containing very small amounts of ammonia is described.

It is essential that the volume of air be measured. Twelve hundred liters of air passed at a rate of 240 liters per hour are sufficient to remove quantitatively the loosely bound nitrogen from egg samples containing from 1.3 to 6.1 mg. of loosely bound nitrogen per 100 grams of sample, using the apparatus and procedure developed in this investigation.

In order to remove quantitatively the loosely bound nitrogen from eggs, in a reasonable and analytically feasible time, the initial pH of the alkalinized egg mixture should be at least 9.5. At pH values higher than 10.7 a continuous decomposition of nonvolatile nitrogenous matter results, yielding ammoniacal nitrogen.

For about 25 years it has been known that hens' eggs will evolve traces of ammonia upon aëration in the cold, after the addition of a small amount of alkali carbonate. The ammonia so liberated has been referred to as ammoniacal or loosely bound nitrogen. The exact measurement of the amount of loosely bound nitrogen recoverable from eggs is accepted as perhaps the best means for grading edible eggs, either as shell eggs direct from the nest or from cold storage, or in the form of frozen egg magmas.

Since distillation of alkalinized egg magma cannot be used, owing to the danger of decomposing the complex nitrogenous compounds present, an application of the Folin aëration method (*4*) for the determination of ammonia in urine has been used for several years in the examination of frozen eggs. It consists essentially in making the sample alkaline, removing the liberated ammonia by aëration, and absorbing it in standardized sulfuric acid solution.

The method as now used is not satisfactory because the operating conditions, chiefly with respect to the volume of air required and the rate of aëration, are not well defined. Until now the nearest approach to a quantitative prescription for the conditions of aëration has been the following:

Hendrickson and Swan (*6*) advised the use of an air pump delivering a pressure of 14 cm. of water. A water gage is connected with the aëration apparatus, keeping the air pressure constant and thus insuring the passage of an equal volume of air through the aëration cylinder in a given time. Redfield (*14, 15*) used an air pump furnishing a blast with a pressure of 10 pounds per square inch and discharging into a tank of sufficient size to compensate for pulsations of the pump and deliver a steady flow. He also insisted on running a blank experiment to determine the percentage recovery of ammonia, using a known amount of pure ammonium sulfate (containing about 3 mg. of nitrogen) and 25 cc. of water. The recovery should be over 95 per cent to be deemed satisfactory. In subsequent reports by Marsh (*11*), Lourie (*9*), and Hertwig (*7*) no details were given concerning the volume of air used in the aëration. Lythgoe (*10*) recommended the use of a pressure sufficient to measure 2 inches (50.8 mm.) of mercury in a manometer attached to the outlet pipe.

Pennington and Greenlee (*13*) applied Folin's method to the determination of loosely bound nitrogen in meat. A small air pump was used to supply the air and the total volume of air passing through a battery of four flasks which contained the alkaline mixture was recorded on an anemometer. This method of measuring does not give the exact volume passing through each individual aëration flask. Kober and Graves (*8*) expressed the need for determining the exact volume of air passing through the ammoniacal mixture and gaged the volume of air by the time it takes for the air to draw a certain volume of water from one bottle to another connected by means of a glass tube. This, however, does not measure the volume of air passing through the ammoniacal mixture, since the resistance offered by the aëration apparatus is so different that the volume of air passing through it in a certain time is by no means identical with the volume of water which would be displaced from one bottle to another in the same time.

Using these methods, checks might be obtained in parallel measurements using the same air pressure and volume, but results could not be duplicated from day to day. The present investigation was undertaken with the object of developing a precise method for the quantitative determination of loosely bound nitrogen in eggs and in whole egg magma. Operating at room temperature, the variables studied were rate of aëration, volume of air, concentration of the aërated alkaline mixture and influence of amount of alcohol therein, and the pH of the alkaline mixture. The need for such a study has recently been asserted by Alfend (*1*).

Aëration Apparatus

For the purpose of providing a flow of air under fairly constant pressure, and measuring the volume of air involved in the aëration of each individual alkaline mixture, the apparatus shown in Figure 1 was developed.

It was found necessary to introduce a pressure regulator into the system. This regulator consisted of two concentric cylinders of galvanized iron, each with one end closed. The outside cylinder, with the open end upwards, had a height of 47.5 inches (121 cm.) and a diameter of 8 inches (20 cm.), and was filled with water to such a height that at the required speed of aëration, air was continuously escaping from the pressure regulator. The inside cylinder was 51.5 inches (131 cm.) high and 2 inches (5 cm.) in diameter. Its top was connected to the air line. It was provided with rectangular holes, *B*, on the lower end to allow the excess air above the required pressure to escape through the water contained in the outside cylinder. This system gave very satisfactory results. An increase of more than 3 to 4 mm. in the difference of water level in the flowmeters was seldom noticed over a period of 6 hours of aëration at 240 liters per hour.

Flowmeters placed between the air line and the aëration cylinders made it possible to evaluate the volume of air passing through each individual cylinder in a given time. The inside diameter and the length of the capillaries sealed in the upper part of the flowmeters were such that a passage of 265 liters of air per hour was possible.

Aëration cylinder *K* containing the ammoniacal mixture was 15 inches (38 cm.) high and 1.875 inches (4.8 cm.) in diameter. The glass tube for aëration extended to within 0.25 inch (6 mm.) from the bottom of the cylinder.

The flowmeters were standardized in the following manner by means of the apparatus shown in Figure 2:

Water was allowed to flow into jar *B*, pinch clamp *G* was opened, the suction pump was turned on, and air was allowed to pass through the aëration apparatus.

Pinchclamp *H* was opened. An extra outlet was introduced to prevent the formation of an air space in the neck of the bell jar to enable the bell jar to be completely filled with water, before the air was allowed to displace the water contained in the jar.

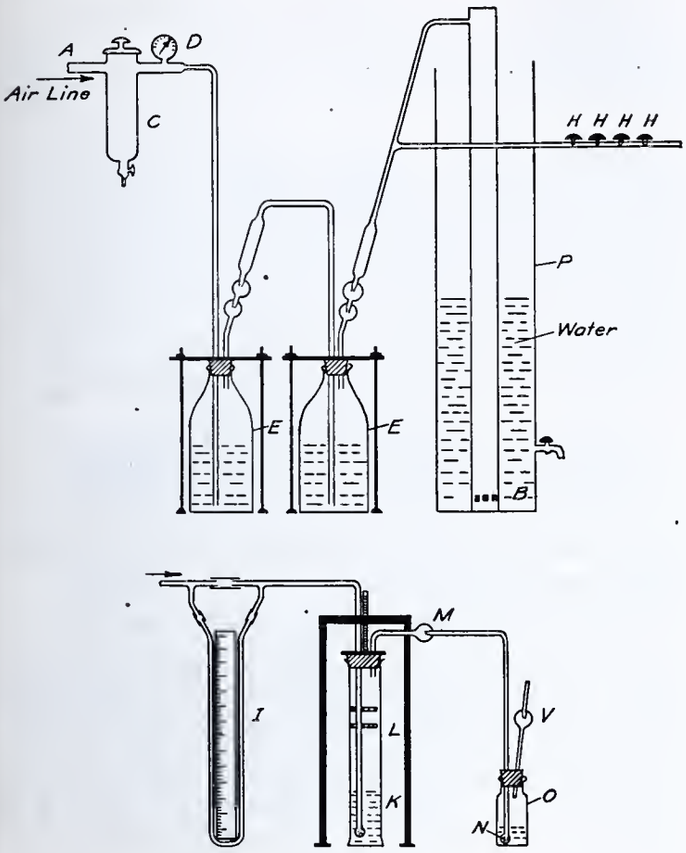

FIGURE 1. AËRATION APPARATUS

A. Air pipe connecting aëration apparatus with air line
C. Air filter
D. Reducing valve permitting reduction of line air pressure to that required for work
E. Wash bottles containing 35 per cent sulfuric acid to remove any ammonia present in air entering apparatus
H. Valves allowing further adjustment of air flow through flowmeters
I. Flowmeters
K. Aëration cylinder
L. Rubber baffles
M. Spray trap
N. Dispersion tube ending with bulb perforated with small holes to allow regular distribution of air through acid solution
O. Receiver containing 10 cc. of 0.02 *N* sulfuric acid diluted with 50 cc. of distilled water
P. Pressure regulator
V. Outlet tube with spray trap

The air was permitted to escape through *H*, thus releasing the pressure at *F*. This permitted the air to flow continuously through the apparatus.

Once the bell jar was filled with water, pinchclamps *G* and *H* were closed and the timing was started by means of a stop watch.

The time necessary to displace the water to the point *F*, corresponding to the atmospheric pressure, was noted. The difference in centimeters was read in the meantime on the flowmeter. Consecutive determinations of time flow were taken at increasing intervals of a 10 cm. difference in water level.

Knowing the volume of the bell jar from the neck to point *F*, it was possible to determine the volume of air passing through the apparatus in a given time and at a given pressure as indicated on the flowmeters.

For each flowmeter the pressure was plotted against the corresponding volume in liters of air passing per hour. In the experiments described, the pressure was observed on the flowmeters and the corresponding volume of air passing per hour through the apparatus was read from the curves.

MATERIAL USED

STANDARD AMMONIUM CHLORIDE SOLUTION. The C. P. salt was recrystallized twice from distilled water, sublimed, and then dried at 105° C. to constant weight. A solution of this salt corresponding to 1.5 mg. of nitrogen per 25 cc. of aqueous solution was prepared and its concentration checked by alkaline distillation into standardized sulfuric acid followed by titration.

POTASSIUM CARBONATE SOLUTION. Fifty grams of potassium carbonate (anhydrous) were made up to 100 cc. with distilled water.

STANDARD SODIUM HYDROXIDE SOLUTION. Using a clear saturated solution of sodium hydroxide, a 0.02 *N* solution was prepared and standardized against Bureau of Standards acid potassium phthalate dried at 105° C. for 2 hours, using phenolphthalein as indicator.

STANDARD SULFURIC ACID SOLUTION. A 0.02 *N* sulfuric acid solution was standardized against the above mentioned sodium hydroxide solution, using methyl red as indicator (0.1 per cent solution in 95 per cent alcohol).

REMOVAL OF AMMONIACAL NITROGEN FROM AMMONIUM CHLORIDE SOLUTION

AS A FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE AMMONIACAL MIXTURE. The percentage of nitrogen recovered as ammonia by aërating alkaline ammoniacal mixtures was carefully investigated first by the use of ammonium chloride solution.

Twenty-five cubic centimeters of 0.02 *N* sulfuric acid were pipetted into the receiver bottle and diluted with 50 cc. of distilled water. Twenty-five cubic centimeters of standard ammonium chloride solution were pipetted into the aëration cylinder and 175 cc. of distilled water added. The cylinders were connected with the receiver bottle and the aëration apparatus.

One cubic centimeter kerosene and 2 cc. potassium carbonate solution were added to the ammoniacal solution. The kerosene was added to prevent foaming. Two cubic centimeters of the potassium carbonate solution were accepted because others found it satisfactory in application to eggs.[1]

The aëration cylinders were closed. The rubber stoppers were screwed down by means of metallic plates. Air was blown through the alkaline ammoniacal solution at different speeds and for different lengths of time. The time of the experiment was noted from the moment that aëration was started until the aëration ended.

Pressure was read on the flowmeters; the corresponding volume of air which passed through the ammoniacal mixture per hour was taken from the curves.

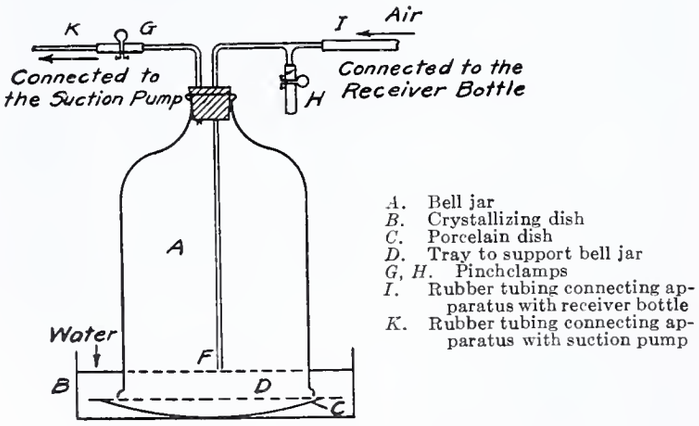

FIGURE 2. APPARATUS FOR STANDARDIZATION OF FLOWMETERS

Once the aëration was stopped, the dispersion tube and the outlet tube were carefully washed with distilled water into the receiver.

The acid solutions were titrated with the standard alkali, using methyl red as the indicator. Two blanks containing 200 cc. of distilled water, 1 cc. of kerosene, and 2 cc. of potassium carbonate solution were run each time.

The difference between the titration of acid solution and of blanks was taken as the measure of the ammoniacal nitrogen carried as a result of the aëration from the alkaline ammoniacal mixture (*K*, Figure 1) into the standard sulfuric acid (*O*, Figure 1).

In all, 119 measurements were made in duplicate at rates of aëration from 124 to 265 liters per hour in the range of 2 to 10

[1] Since the apparatus contained no provision for the removal of carbon dioxide from the air, the following experiment was performed: Eighty cubic centimeters of potassium carbonate solution were added to 520 cc. of distilled water. The pH of this solution was found to be 11.2. Then two portions of 150 cc. each, plus 1 cc. of kerosene, were aërated 5 hours at a rate of 240 liters of air per hour. The pH was then found to be 10.5. Obviously the use of the amount of potassium carbonate specified insures an alkaline reaction.

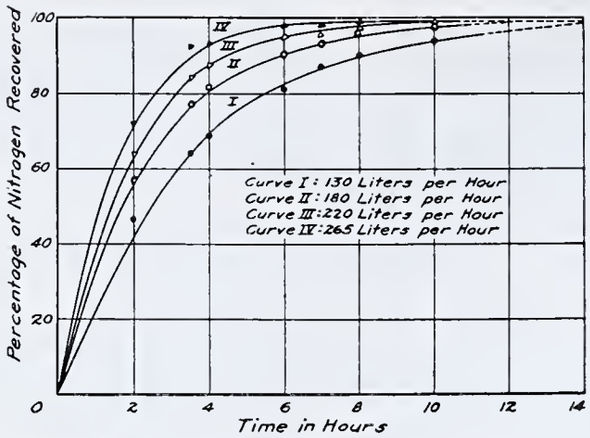

FIGURE 3. AMMONIACAL NITROGEN RECOVERED AS FUNCTION OF LENGTH OF TIME AT INCREASING RATES OF AËRATION

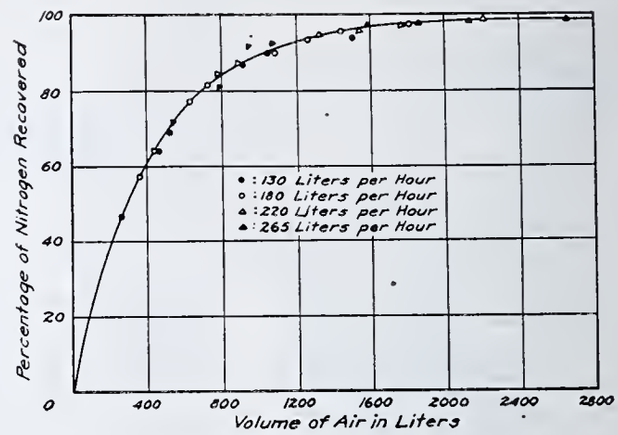

FIGURE 4. AMMONIACAL NITROGEN RECOVERED AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE MIXTURE AT INCREASING RATES OF AËRATION

hours' aëration. The data obtained in these experiments are summarized in Figures 3 and 4. The curves in Figure 3 show that the percentage of nitrogen recovered is a function of the length of time of aëration, that about half of the ammonia comes over in the first 2 hours, and that a very large volume of air is necessary to remove the last traces of ammonia.

Figure 4 shows conclusively that the percentage of nitrogen recovered is primarily a function of the volume of air which passes through the ammoniacal mixture, since all the results obtained by aëration at different speeds for increasing length of time fall on the same curve. This means that a definite volume of air, regardless of the speed of aëration in the range considered (135 to 265 liters of air per hour), will liberate a definite amount of ammonia from an ammonium chloride solution treated in the manner described.

There are three main drawbacks to increasing the speed of aëration above 270 liters of air per hour with the apparatus used: At a higher speed the alkaline ammoniacal mixture may be carried over mechanically into the receiver; the acid solution may be blown out of the receiver; and the absorption of the ammonia may not be complete in the standard acid.

To prevent particles from being sprayed over mechanically into the receiver, the glass tubes connecting the aëration cylinder and the receiver bottle were fitted with a glass trap. Rubber baffles were placed on the aëration tubes inside the cylinder for the same purpose. At the highest speed of aëration of 270 liters per hour as used in some experiments, controlled blank tests showed that no acid solution was blown out of the receiver.

To investigate the absorption of the liberated ammonia in the receiver containing the acid solution, a second receiver, containing 10 cc. of standard sulfuric acid and 50 cc. of water, was placed in series with the first. The other conditions were the same as above. The titration of the solution in the second receiver in each experiment and of that in the blank checked within the precision of the method. Hence at a rate of aëration of 270 liters per hour the absorption of liberated ammonia is complete in the acid solution contained in the first receiver.

AS A FUNCTION OF VOLUME AND CONCENTRATION OF AMMONIACAL MIXTURES. Folin and Macallum (*5*) called attention to the fact that the rapidity with which a given air current removes ammonia from solutions depends on the volume of the solution. The extent of the influence of volume is shown by curves I and II in Figure 5.

The conditions represented by the curve I experiment cannot be applied to eggs owing to the high viscosity. Use of alcohol as a diluent has been found necessary in order to inhibit foaming. Since ammonia is five times less soluble in alcohol than in water, the ammonia should be removed more rapidly, as shown by comparison of curves II and III.

REMOVAL OF LOOSELY BOUND NITROGEN FROM EGGS

The best conditions for the determination of ammoniacal nitrogen in eggs were investigated with respect to the weight of sample, total volume of alkaline egg mixture, and volume of alcohol and water added. The mixture which was found to give the least mechanical disturbances, such as splashing and sticking to the sides of the cylinder, and the order of preparation of the alkaline mixture prior to aëration were as follows:

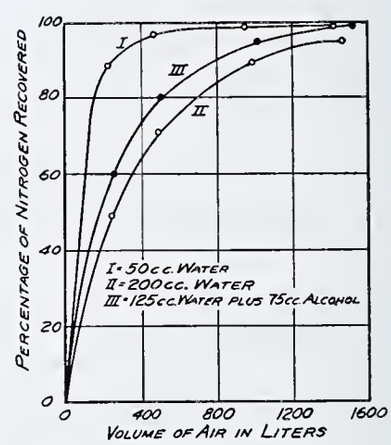

FIGURE 5. INFLUENCE OF VOLUME OF AQUEOUS SOLUTION AND OF SUBSTITUTION OF ALCOHOL FOR WATER ON RECOVERY OF AMMONIA

Ammonium chloride equal to 1.5 mg. of nitrogen present in each case.

One gram of sodium fluoride was put in the aëration cylinder. Twenty-five grams of mixed egg specimen weighed by difference in a weighing bottle were put in the aëration cylinder. The contents of the cylinder were then diluted with distilled water, the volume of added water being 75 cc. minus the number of cubic centimeters of potassium carbonate solution added later.

Fifty cubic centimeters of 95 per cent ethyl alcohol were added and then 1 cc. of kerosene. Kerosene and alcohol are essential as foam breakers. The potassium carbonate solution was added last when the whole apparatus had been connected, and the aëration was immediately started.

AS A FUNCTION OF TOTAL VOLUME OF AIR PASSED THROUGH ALKALINE EGG MIXTURE. The eggs used in these and subsequently described experiments were carefully selected at a storage and egg-breaking plant in Jersey City, N. J.

Specimen I consisted of storage eggs which had been kept at 30° to 32° F. (−1.1° to 0° C.) for 4 months. After removal from the shells, approximately 35 pounds (16 kg.) of the whole egg mixture were passed through a colloid mill to obtain a uniform magma which would not thicken on frozen storage (*3*). This well-mixed egg magma was poured into half-pint jars which were placed immediately in the storage room at −5° to 0° F. (−21° to −18° C.).

Specimen II consisted of fresh eggs carefully selected and broken out of the shell, then mixed and stored in the same manner as specimen I.

As needed, samples were delivered from Jersey City on the evening prior to their use and were stored overnight in the labora-

tory at 0° to 20° F. (−18° to −7° C.). Immediately before weighing out the samples, the frozen specimens were thawed by immersing the jars in the water of a thermostat at 25° C. During the thawing, which was completed in 20 minutes, the contents were stirred continuously.

Using specimen I with 2 cc. of the potassium carbonate solution as the alkalinizing agent, the influence of the rate of aëration at various times was measured. The results, plotted as curve I in Figure 6, lead to the conclusion that the recovery of loosely bound nitrogen is primarily a function of the total volume of air passed through the alkaline egg mixture and is independent of the speed of aëration in the range considered, since all the results obtained for different speeds fall on the same curve, just as was found for ammonium chloride solutions.

The only advantage of increasing the velocity of aëration is shortening the time of the experiment. Inasmuch as a speed of 240 liters per hour allows complete absorption of the liberated ammonia in the 0.02 *N* sulfuric acid and does not cause any blowing out of the acid solution from the receiver or any mechanical carrying over of particles from the aëration cylinder to the receiving bottle, this rate of aëration was used in the subsequent experiments. Satisfactory precision was obtained, as may be seen from Table I, using egg specimen II, aërating at 240 liters of air per hour for 5 hours, and using 2 cc. of potassium carbonate solution containing 50 grams of potassium carbonate per 100 cc. of solution. Curve I in Figure 6 seems to indicate that 1200 liters of air are sufficient, since further aëration failed to remove more ammoniacal nitrogen.

Experiments were then performed to determine whether this volume of air passing at 240 liters per hour would be sufficient to recover the loosely bound nitrogen from egg samples containing smaller or greater amounts than specimen I.

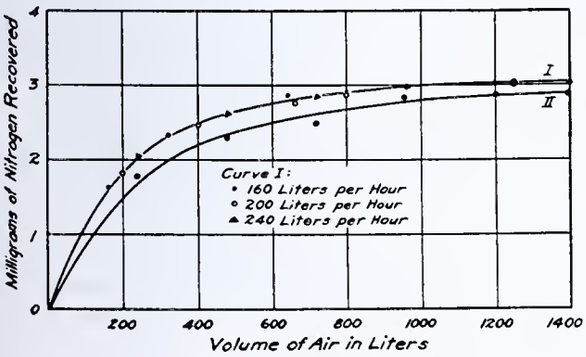

FIGURE 6. REMOVAL OF AMMONIACAL NITROGEN AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE MIXTURE

I. Ammoniacal nitrogen recovered from egg sample I, expressed in milligrams of nitrogen per 100-gram sample.
II. Ammoniacal nitrogen recovered from standard ammonium chloride solution, expressed in milligrams of nitrogen per 100 cc. of solution.

Figure 7 gives the results obtained from different samples. Specimens I, II, Ib, and Ic were analyzed under the same conditions, using 2 cc. of potassium carbonate solution as alkaline reagent. Specimens Ib and Ic were prepared by merely keeping specimen I at 45° F. (7° C.) for 39 and 63 hours, respectively, thus permitting slight decomposition to take place. Inspection of Figure 7 shows that additional aëration above 1200 liters failed to remove any more ammoniacal nitrogen, since the curve flattens out; the tangent to the curve at the point corresponding to 1200 liters of aëration is practically parallel to the abscissa. This flattening out of the curve, which in the case of aëration of ammoniacal nitrogen from a standard ammonium chloride solution corresponds to 99.0 ± 0.5 per cent of the actual nitrogen present, has in the case of the determination of loosely bound nitrogen in egg still another significance. It is possible that the presence of the added potassium carbonate catalyzes the hydrolysis of the egg magma with the consequence that more ammonia is split off, which is then determined as ammoniacal nitrogen. The flattening out of the curve proves that, if there is any such hydrolysis, it is not continuous.

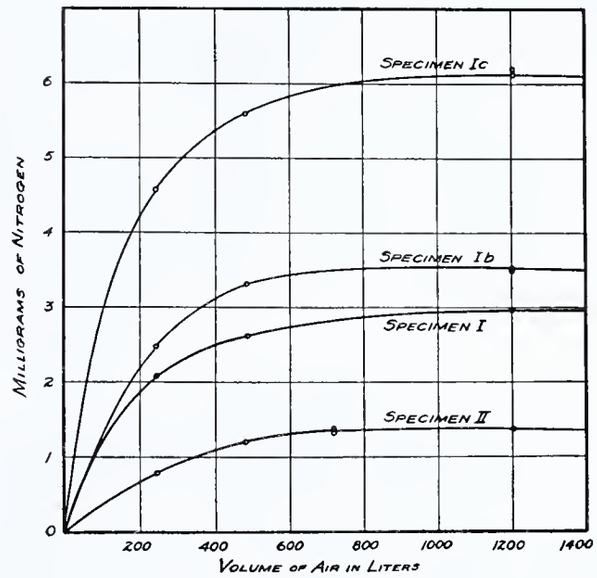

FIGURE 7. REMOVAL OF AMMONIACAL NITROGEN FROM EGGS AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE EGG MIXTURE

AS A FUNCTION OF CONCENTRATION OF POTASSIUM CARBONATE. First the influence of different amounts of potassium carbonate upon the pH of the solutions was measured by means of the modified Bailey electrodes (*2*, *3*). The solutions consisted of 25 grams of egg specimen II, 1 gram of sodium fluoride, 75 minus *x* cc. of distilled water, and *x* cc. of potassium carbonate solution. Figure 8 summarizes the results.

TABLE I. PRECISION OF MEASUREMENTS

Frozen-Storage Age	Loosely Bound Nitrogen	Number of Experiments	Average Deviation Single observation[b]	Average Deviation Mean[c]
Days[a]	*Mg./100 g.*			
7	1.34	5	0.04	0.02
8	1.41	6	0.02	0.01
9	1.37	6	0.02	0.01
10	1.25	5	0.04	0.02
11	1.14	6	0.04	0.02
14	1.05	6	0.04	0.02
16	1.32	4	0.02	0.01
17	1.38	4	0.02	0.01
21	1.34	5	0.04	0.02
24	1.33	5	0.02	0.01
25	1.35	2	0.00	0.00
26	1.31	4	0.01	0.006
27	1.34	4	0.01	0.005
30	1.35	5	0.01	0.005
31	1.35	6	0.02	0.01
36	1.38	6	0.01	0.005
48	1.37	3	0.01	0.008

[a] Number of days specimen was kept at 0°F. (−18° C.) prior to analysis.
[b] Sum of the deviations of each individual measurement from the arithmetical mean divided by the number of experiments.
[c] Average deviation divided by the square root of the number of experiments.

Then in order to measure the influence of the concentration of potassium carbonate on the liberation and removal of ammoniacal nitrogen, a series of experiments was performed which are summarized in Figure 9.

From curve 0 it is obvious that an alkaline reagent must be added in order to speed up the recovery of the ammoniacal nitrogen. Curves 0.5 to 12, inclusive, show that upon increasing additions of potassium carbonate solution, increasing quantities of ammoniacal nitrogen are recovered. These curves also indicate that it is necessary to aërate the egg mixture at an initial pH of at least 9.5 in order to obtain a quantitative recovery of ammoniacal nitrogen originally present.

They suggest, too, that more than 4 cc. of potassium carbonate solution should not be used to effect a definite end point for an analytically reasonable expenditure of time and effort. Curves 8 and 12 may be interpreted as showing that the corresponding amounts of potassium carbonate catalyze a hydrolytic decomposition of complex nitrogenous substances into volatile basic nitrogen compounds.

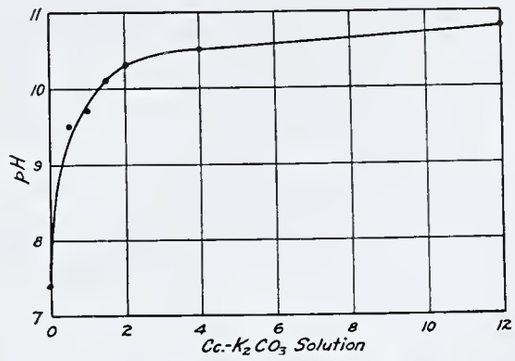

Figure 8. pH of Aqueous Egg Mixture, as Function of Amount of Potassium Carbonate Solution Added

It is known that increasing alkalinity as effected by use of sodium hydroxide yields increasing amounts of ammoniacal nitrogen from eggs (*6*). Also, increasing amounts of sodium carbonate producing pH values over 9.0 have been shown to cause decomposition of amino acids at about 100° C. (*12*). Results such as those represented by curves 0.5, 2, and 4 in Figure 9 have not been heretofore demonstrated. The selection of any of these three conditions is indicated as proper for the purpose and consequently it is well to adhere to the previous empirical selection of potassium carbonate solution, giving an initial pH of about 10.3.

Validity and Use of Standard Ammonia Controls

It has been customary with some workers to run parallel aërations of an ammonium chloride or ammonium sulfate solution to serve as a gage of the efficiency of the analysis of an egg specimen. If over 95 per cent of the actual amount of nitrogen present in the solution was recovered, it was concluded that approximately the same percentage of ammoniacal nitrogen present in the egg sample had been recovered. However, such a conclusion is possible only when the percentage of the ammoniacal nitrogen is approximately the same in both egg mixture and ammonium chloride solution and when all other conditions are identical.

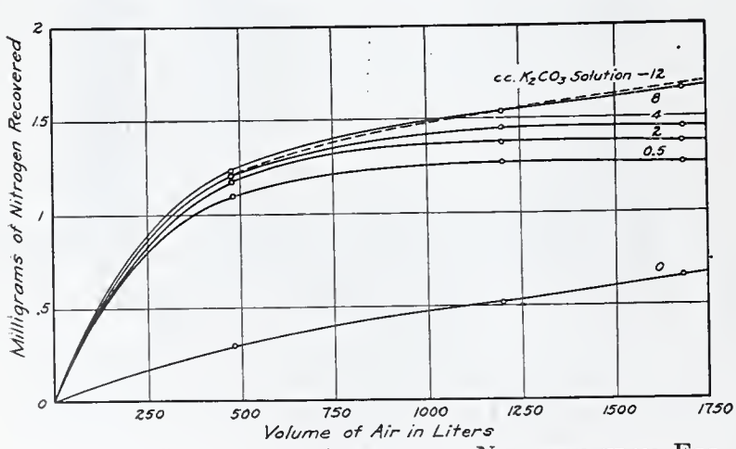

Figure 9. Removal of Ammoniacal Nitrogen from Egg Mixtures Containing Varying Amounts of Potassium Carbonate

Since egg specimen I contained approximately 3 mg. of ammoniacal nitrogen per 100 grams, the ammoniacal nitrogen was evaluated in a standard ammonium chloride solution containing 2.99 mg. of nitrogen per 100 cc. of solution by blowing air at a rate of 240 liters per hour, using 2 cc. of potassium carbonate solution as alkaline agent. The results obtained are plotted in curve II of Figure 6. Curves II and I are converging; the liberation of ammoniacal nitrogen in eggs is similar to that of standard ammonium salt solutions, when the percentage of ammoniacal nitrogen is approximately the same and when the conditions of the experiment are the same. This investigation shows, however, that when the conditions of rate and time of aëration, pH, and volume of the egg mixture are controlled, it is unnecessary to run ammonium salt controls.

Details of Method

As a result of this investigation, the authors recommend the following method for the precise determination of the loosely bound nitrogen in eggs, using the apparatus described in Figure 1:

Measure accurately 10 cc. of 0.02 *N* sulfuric acid into the receiver, *O*, and dilute with 50 cc. of distilled water. Place 1 gram of sodium fluoride in aëration cylinder *K*. Pour 25 grams of mixed egg magma, weighed by difference from a weighing bottle, into the aëration cylinder. Add 55 cc. of distilled water, 50 cc. of ethyl alcohol (95 per cent by volume), and 1 cc. of kerosene.

Connect the cylinders with the receiver bottle and the aëration apparatus. Add 20 cc. of potassium carbonate solution, containing 5 grams of anhydrous potassium carbonate per 100 cc. of solution. Close the aëration cylinders, and start the aëration, allowing the passage of 1200 liters of air at a rate of 240 liters per hour.

Titrate the excess of acid with 0.02 *N* sodium hydroxide (free from carbon dioxide) by means of a microburet which can be read to 0.01 cc.

Run at the same time two blank experiments, containing 1 gram of sodium fluoride, 80 cc. of distilled water, 50 cc. of 95 per cent alcohol, 1 cc. of kerosene, and 20 cc. of potassium carbonate solution.

Take the difference between the titration of excess acid and of blanks as the measure of the ammoniacal nitrogen carried as a result of the aëration from the alkaline egg mixture, *K*, into the standard sulfuric acid, *O*. Express the results obtained as milligrams of "ammonia nitrogen" per 100 grams of sample.

From a consideration of all the errors involved in the above method, the precision is indicated to be ±2 per cent.

Acknowledgment

The authors wish to express their indebtedness to Samuel B. Ellis for his coöperation in the construction and standardization of the flowmeters used.

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Spectral Determination of Fluorine in Water

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THE occurrence of fluorine in potable waters and the probabilities of its physiological effect have aroused considerable interest in the past few years. Churchill (*1*), Dean (*2*, *3*), Sebrell, Dean, Elvore, and Breaux (*8*), Kempf and McKay (*4*), Smith, Lanz, and Smith (*9*), and others have made comprehensive investigations on the subject. The general interest has stimulated activity among analytical chemists toward the development of methods for the accurate estimation of fluorine in the quantities which occur in natural waters. The amounts reported have varied from zero to as much as 14 p. p. m. of fluorine. Among the recent developments are the works of Willard and Winter (*11*), Thompson and Taylor (*10*), Sanchis (*7*), and Kolthoff and Stansby (*5*).

Figure 1. Electrode Holder Partially Filled with Electrodes

Under certain conditions, difficulties which are not easily obviated, may be encountered in the chemical determination of fluorine in water. For this reason, the possibility of using spectral methods for the determination has been investigated in Aluminum Research Laboratories.

Description of Method

The detection or estimation of fluorine in any material by spectral methods is based on the appearance of the band spectrum of calcium fluoride when a substance containing both fluorine and calcium is excited in the electric arc or spark. The band with head at λ5291 is the most sensitive and is the one the author has used for the examination of water. Papish, Hoag, and Snee (*6*) have made use of the band spectrum of calcium fluoride for the detection of fluorine in gems and other minerals. Fluorine may be detected either by the photographing or visual observation of its spectrum. When the dissolved mineral matter consists essentially of calcium and magnesium compounds, the estimate can usually be made by arcing the dry residue. However, when large amounts of sodium compounds are present, calcium must be supplied externally. The most dependable means found in these laboratories for supplying the calcium is the impregnation of the lower electrode which supports the sample, with calcium chloride. The calcium salt in the electrode eliminates the variable intensities which result from the more or less selective volatilization of the various constituents of saline water residues.

Apparatus

Aluminum Research Laboratories has available a large Littrow quartz spectrograph and a Hilger constant-deviation spectrometer, either of which may be used for the detection and estimation of fluorine. The spectrometer may be used visually or photographically. In a large part of the experimental work on fluorine both the quartz spectrograph and the glass spectrometer were used simultaneously, recording the spectra with the spectrograph while observing visually the performance of the fluorine bands with the spectrometer. By this means the author was enabled to reach the decision that visual estimates are possible where the base of the water residue is essentially calcium and magnesium compounds, but that photographic methods are necessary with saline residues. All spectrograms are examined by projection upon an aluminum screen by means of a Bausch and Lomb lantern slide projector. The projector has been equipped with a special plate holder to fit the 3 inch (7.62 cm.) × 10 inch (25.4 cm.) spectrograms, and the lens mount has been extended for short-range projection.

Experimental

By a study of the spectrum of calcium carbonate containing known added amounts of fluorine, it has been found that when photographed the calcium fluoride band will show a satisfactory density gradient when the fluorine lies between the approximate limits of 0.05 and 1.5 per cent of the calcium carbonate when using a sample weighing 12.5 mg. By varying the amount of material used for the arc, the limits can probably be broadened. For water analysis this range is satisfactory. The series of standards used for this investigation were prepared to contain 0.025, 0.05, 0.10, 0.25, 0.50, 1.00, 1.50, and 2.00 per cent of fluorine. When examined visually during the burning of the sample, the calcium fluoride band was found to disappear after a few seconds, the time varying with the amount of fluorine present. By plotting the time in seconds against the percentage of fluorine in the base material, a satisfactory curve can be drawn. For analysis of water of the same approximate composition as the standards used for plotting the curve, the estimate requires only the observation of the time required for the disappearance of the calcium fluoride band.

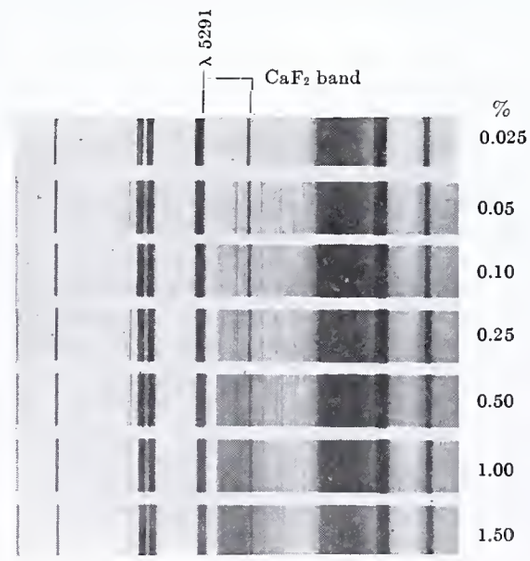

Figure 2. Spectra of Standards Containing Various Amounts of Fluorine

Some of the western waters examined contained as much as 2000 p. p. m. of dissolved solids, mainly sodium chloride. With these waters, the best arc performance resulted when specially prepared electrodes were used. The electrodes, 0.25 inch (6.35 mm.) diameter graphite, were prepared by

cutting to 1.25-inch (31.8-mm.) lengths. A shallow cavity, about 0.078 inch (1.98 mm.), was drilled in one end of half the electrodes. The other half, to serve as upper electrodes, were not drilled, nor were they impregnated. The drilled electrodes were placed in a 50 per cent solution of calcium chloride and under a bell jar which was then evacuated in order to fill the voids of the graphite with the solution. When no air bubbles were observed at the surface of the electrodes, they were removed from the jar and the calcium chloride, dried in an oven at 175° C., and stored in a desiccator.

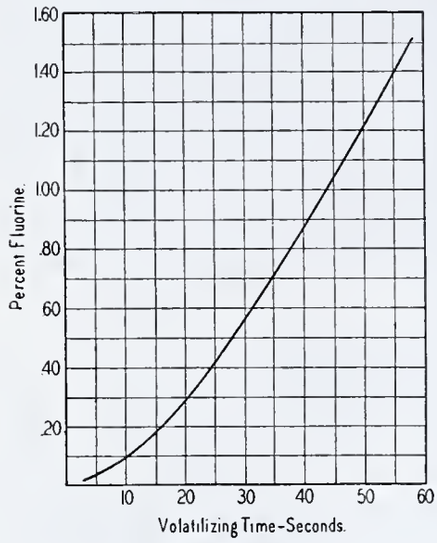

Figure 3. Curve for Estimating Fluorine by Visual Observation

Standards

For the preparation of standards, c. p. calcium carbonate may be used as the base. Freedom from fluorine is first assured by a spectral analysis of the calcium carbonate. Fluorine in suitable amounts is added from an aqueous solution of a fluorine salt. Sodium or calcium fluoride may be used, although sodium fluoride is preferable because of its greater solubility. Both sodium and calcium fluoride have been used in these laboratories, since there is some doubt about the combination of the fluorine as it exists in water. However, the agreement in results of fluorine determined using either salt is such that the choice is considered as optional.

A few grams of calcium carbonate are pulverized to a fine powder in an agate mortar. The desired amount is weighed from the ground material and placed in a platinum dish. The fluorine solution is next added and the volume diluted to approximately 100 cc. This solution is evaporated to dryness in any convenient manner. The residue is removed from the dish and thoroughly ground to insure intimate mixing of the calcium carbonate and fluorine salt. The entire series is usually prepared at one time, adjusting all volumes to 100 cc. before evaporation.

A word regarding the preparation of special standards may be desirable at this point. In any spectral analysis where an estimate of quantity is desired, it is essential that the composition of the standards and the sample under investigation be very similar. If the mineral residue of a water is radically different from the typical calcium carbonate residue, a set of standards should be prepared, the base of which approximates that of the water residue itself. This information is usually available from the chemical analysis of the water. If such analysis cannot be obtained, the spectrographic analysis of the residue will establish the metals and simple chemical tests can be made to identify the acid radicals.

Analysis of Samples

Since the spectral method for fluorine in water consists of estimating the fluorine in the residue, it becomes apparent that the sensitivity of the test depends largely on the ratio of fluorine to residue. The experimental work has shown that the accurate range for estimating the fluorine extends from 0.05 to 1.5 per cent of the residue. For a great many waters all that is needed may be evaporation of the water to dryness and immediate examination of the residue. However, there may often be cases where the fluorine is present in too great a quantity to allow direct use of the residue, and dilution will be necessary. For example, assuming that a water contains 200 p. p. m. of "ignited residue," fluorine between 0.1 and 3.0 p. p. m. could be estimated by evaporating the necessary volume to provide the required amount of residue. If such a water contained more than 3.0 p. p. m. of fluorine, the addition of calcium carbonate as a diluent would be necessary to reduce the fluorine to a determinable amount. Electrodes impregnated with calcium chloride are satisfactory for any water and in order to avoid any shortage of calcium are recommended for all analyses.

Procedure: Evaporate enough of the water in a platinum dish to provide 50 mg. of ignited residue. Standard methods of water analysis should be followed in all details except in the quantity of water used for the sample. The ignited residue is merely the mineral matter which is left after the organic matter has been decomposed. A temperature of 500° C. is used for the ignition. Remove the residue from the dish with the aid of a wood spatula, using a little distilled water if necessary. If water is used, the residue must of course be dried. Transfer the residue to an agate mortar and pulverize thoroughly. Pulverizing is essential for a thoroughly homogeneous sample. Place 12.5 mg. of the pulverized residue in the cavity of the calcium impregnated graphite electrode, packing in tightly. A convenient method of filling the electrodes is to deposit the residue on a flat surface and place the electrode over the sample, cavity downward, in a manner similar to that used by druggists for filling gelatin capsules. This usually results in a very satisfactory electrode.

Place the filled electrode in the arc stand, using a solid unimpregnated upper electrode. The lower electrode containing the sample is the anode of the circuit. If the photographic method is being used, burn the residue until it has been completely volatilized. This will require about one minute with a current of 15 amperes. The time will of course vary, depending upon the composition of the residue. If a visual determination is being made, the current is interrupted as soon as the calcium fluoride band disappears. All determinations should be made in duplicate.

Develop the plate if the spectrograph was used, and project the spectrum, matching the intensities of the calcium fluoride bands with those of the standards. Since the difference between adjacent standards is not great, estimation to the nearest standard will usually be sufficiently accurate. Interpolation is possible if greater accuracy is desired.

Because some residues have been found to be slightly hygroscopic, the filled electrodes are placed in an aluminum holder drilled with holes to fit the electrodes. The holder is kept at a temperature of about 200° C. by a gas flame. This precaution often prevents considerable annoyance and delay from the loss of a sample, which is likely to happen if the residues pick up a little moisture. Figure 1 shows the holder filled with electrodes.

Reproduction of the spectra of a series of fluorine standards is shown in Figure 2. The gradation is clearly evident, although considerable detail is lost in the various stages of reproduction. This set was synthesized for determining the fluorine in a certain water containing 200 p. p. m. of residue, principally calcium carbonate. The amounts of fluorine are 0.025, 0.05, 0.10, 0.25, 0.50, 1.0, and 1.5 per cent of the residue, or, respectively, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, and 3.00 p. p. m. of fluorine in the water. This same set of standards would serve for the estimation of fluorine in other waters whose residues are similar, by calculation of the amount of fluorine in the residue to a water basis.

Figure 3 is a curve typical of the results derived from the visual examination of fluorine-bearing waters. When the water residue is such that the visual instrument can be used, this affords the most rapid means of making the determination.

Summary

Spectral methods for estimating fluorine in the mineral residue of water have been found to yield satisfactory results.

Photographic methods are suitable for all waters. Visual

methods are satisfactory for waters whose residues consist essentially of calcium and magnesium.

The conditions for most accurate estimation exist when the fluorine is between 0.05 and 1.5 per cent of the residue.

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Analytical Uses of 2-Propanol

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In considering 2-propanol as a substitute for ethanol in analytical procedures there are relatively few unfavorable factors. There is very little difference in the physical properties of the two alcohols.

As a solvent for analytical reagents, particularly organic reagents, 2-propanol is a satisfactory substitute for ethanol. For inorganic reagents in rather high concentrations the absolute alcohol must be used, since two liquid phases are formed with the constant-boiling mixture.

As a reagent for the qualitative detection of certain elements or radicals 2-propanol is not effective, especially where the chemical properties of the alcohol are significant. Thus the flame test for boron and the ester test for acetates fail to work with 2-propanol.

Certain inorganic compounds can be separated with 2-propanol. The advantage of the lower solubility of salts in 2-propanol is canceled by the decreased solubility of the soluble as well as the insoluble salt. However, 2-propanol is a satisfactory substitute for ethanol in this type of separation, and can be used in determinations to decrease the solubility of precipitates, and as a washing medium for precipitates.

THE extent and variety of the uses of ethanol in analytical chemistry, indicated in a preliminary paper (*7*), include the preparation of materials for analytical work, such as analytical devices, reagents, and samples; and the determination of constituents, involving reactions such as the separation of materials, the reduction of the solubility of precipitates, and the removal of adhering liquids.

In view of the cost of ethanol (including tax) and of the inconvenience of the precautions necessary to prevent its diversion, it would be of advantage to find a suitable substitute. The selection of such a substitute should be made on the basis of low cost and of similarity in properties. Of the lower members of the series of aliphatic alcohols having physical and chemical properties similar to those of ethanol, 2-propanol is most nearly like ethanol. It is completely miscible with water and recent commercial production has brought the price considerably lower than that of taxed ethanol. The data in Table I, obtained from International Critical Tables, indicate the great similarity in the properties of these two compounds.

TABLE I. PHYSICAL PROPERTIES OF ETHANOL AND 2-PROPANOL

PROPERTY	ETHANOL	2-PROPANOL
Boiling points, at 760 mm.	100% C_2H_5OH, 78.4° C. B. C_2H_5OH, 78.15°	100% C_3H_7OH, 82.26° C. B. C_3H_7OH, 80.37°
Heat of combustion	328 kg.-cal./mole 7.13 kg.-cal./gram	474.8 kg.-cal./mole 7.91 kg.-cal./gram
Heat of vaporization at boiling point	855 joules/gram	667 ± 2% joules/gram
Vapor pressure at 20° C.	43.9 mm. Hg	32.4 mm. Hg
Refractive index. Na D line	1.36242 at 18.35° C.	1.37757 at 20° C.
Surface tension at 20° C.	22.27 ± 0.1	21.7 ± 0.3
Viscosity	1.716×10^{-2}	2.101×10^{-2}

As a laboratory reagent 2-propanol has had some application. Griffin (*10*) successfully substituted it for ethyl alcohol in histological work, the preparation of reagents, and general laboratory use. Gilson (*8*) states, "During several years of biochemical research the writer has found many instances where isopropanol could be substituted for ethanol in laboratory work. It is cheap and there are no restrictions governing its use, nor is it likely to be an object of theft." Schuette and Smith (*18*), using 2-propanol in the determination of acid numbers, obtained more satisfactory results than with ethanol. Schuette and Harris (*17*) made the same substitution in the determination of saponification numbers, using 2-propanol in the preparation of solutions of potassium hydroxide.

In references to the use of 2-propanol as a substitute for ethanol, there are few data of value in predicting its applicability as an analytical reagent. Neither International Critical Tables nor Seidell's "Solubilities of Inorganic Compounds" contains any appreciable amount of information regarding the solubility of inorganic salts in isopropyl alcohol, data which would be of importance in predicting the behavior of the reagent in inorganic analysis.

Four articles have recently been published regarding the solubility of compounds in 2-propanol. Kirn and Dunlap (*13*) studied the solubilities of the alkali chlorides and sulfates in anhydrous alcohols, including isopropyl alcohol. These salts are slightly more soluble in ethanol than in 2-propanol. Ginnings and Chen (*9*) investigated the ternary systems, water, 2-propanol, and salts, obtaining qualitative results with seventy-five common inorganic salts and quantitative results with ten salts. Hopkins and Quill (*12*), in a study of the use of nonaqueous solvents in the rare earth group, stated that isopropyl alcohol is a very poor solvent for the rare earth chlorides. In determining the solubility of silver bromate in mixtures of alcohols and water Neuman (*15*) found that the values in mixtures of isopropyl alcohol and water fall between those in ethanol-water mixtures and those in *n*-propanol-water mixtures.

Table II. Determination of Nickel and Copper

Element Determined	Amount Present	Ethanol Solution of Reagent Found	2-Propanol Solution of Reagent Found
Nickel with dimethylglyoxime	0.0564	0.0559	0.0560
		0.0559	0.0560
		0.0559	0.0560
		Av. 0.0559	Av. 0.0560
Copper with 8-hydroxyquinoline	0.1052	0.1054	0.1054
		0.1052	0.1053
		0.1053	0.1054
		Av. 0.1053	Av. 0.1054

Table III. Solubility of Sodium and Potassium Chlorides in Ethanol

(Grams of salt per 100 grams of solvent)

Salt	Temp. °C.	Per Cent Alcohol by Weight 86.4	89.6	92.3	96.9	100
KCl	16	....	0.1413	0.0865	0.0432	0.0263
		0.2256	0.1415	0.0860	0.0431	0.0268
KCl	25	0.2777	0.1744	0.1085	0.0502	0.0291
		0.2780	0.1743	0.1082	0.0499	0.0286
KCl	35	0.3139	0.1997	0.1203	0.0599	0.0325
		0.3130	0.1992	0.1212	0.0605	0.0326
NaCl	16	0.5771	0.3712	0.2369	0.1187	0.0657
		0.5763	0.3710	0.2346	0.1179	0.0656
NaCl	25	0.6414	0.4184	0.2671	0.1221	0.0657
		0.6420	0.4179	0.2669	0.1218	0.0658
NaCl	35	0.6582	0.4345	0.2708	0.1338	0.0667
		0.6590	0.4345	0.2705	0.1331	0.0666

Table IV. Solubility of Sodium and Potassium Chlorides in 2-Propanol

(Grams of salt per 100 grams of solvent)

Salt	Temp. °C.	Per Cent Alcohol by Weight 87.7	92.6	96.5	100
KCl	16	0.1099	0.0284	0.0078	0.0023
		0.1092	0.0289	0.0071	0.0029
KCl	25	0.1279	0.0300	0.0084	0.0026
		0.1281	0.0296	0.0085	0.0029
KCl	35	0.1494	0.0362	0.0102	0.0029
		0.1495	0.0366	0.0107	0.0029
NaCl	16	0.2647	0.0645	0.0175	0.0040
		0.2652	0.0649	0.0164	0.0039
NaCl	25	0.2810	0.0632	0.0157	0.0041
		0.2813	0.0629	0.0166	0.0041
NaCl	35	0.2968	0.0697	0.0183	0.0031
		0.2967	0.0705	0.0184	0.0029

Experimental Work

Preparation of Materials. The constant-boiling alcohols were purified by a single distillation of the commercial product through a 40-cm. Vigreux distilling column. The 2-propanol had a density (d_4^{25}) of 0.8120, corresponding to an 87.7 per cent solution by weight; the respective values for the ethanol were 0.8062, and 92.3 per cent. The 98 to 99 per cent commercial alcohols were dehydrated by refluxing for 24 hours over calcium oxide. At the end of this period they were distilled through the 40-cm. column. The density (d_4^{25}) of the 2-propanol was 0.7807 and that of the ethanol 0.7846.

The salts used for the determination of solubilities were purified by double recrystallization. The reagents used were prepared from the usual reagent quality chemicals.

General Use. The use of alcohol in the preparation of analytical devices depends almost entirely upon its physical properties. No experimental work was done with 2-propanol in this connection; however, there seems to be no reason why it should not be used in cleaning apparatus, in washing crucibles, and in similar ways, since its physical properties are much like those of ethanol.

Use as a Solvent. Quite frequently the organic reagents used in analytical work are insoluble in water. In such cases the most common solvent is ethyl alcohol. Unless the presence of 2-propanol has a detrimental effect in determinations where alcoholic solutions of reagents are used, the only question as to its applicability is its ability to dissolve the reagents.

Solutions of dimethylglyoxime, 8-hydroxyquinoline, and alpha-benzoinoxime were prepared in 91 per cent 2-propanol and 95 per cent ethanol. The dimethylglyoxime was prepared as a 1 per cent solution and the other two reagents as 2 per cent solutions. No difficulty was encountered in preparing solutions of this concentration, although the reagents dissolved more slowly in the 2-propanol than in ethanol.

In order to determine whether there might be any difference in the effect of 2-propanol and ethanol on the actual determinations, the solutions of dimethylglyoxime were used for the precipitation of nickel and those of 8-hydroxyquinoline for the precipitation of copper, with the results shown in Table II.

In the case of inorganic reagents the application of 2-propanol as a solvent is somewhat limited by the fact that it is salted out by many inorganic compounds. This eliminated the 91 per cent alcohol from consideration except for dilute solutions of reagents.. Absolute 2-propanol has been used as a solvent for potassium hydroxide by Schuette and Harris (*17*) and Schuette and Smith (*18*) in the determination of acid and saponification numbers. The latter authors state that a yellow color can be avoided by allowing solution to take place without the application of heat. In the present work a yellow color appeared with 2-propanol after a relatively short time in a 0.5 *N* solution of this base, although no heat was applied to hasten solution. The color developed when the solution was stored in the dark as well as in the light. However, a 0.1 *N* solution prepared in a similar manner remained colorless. The hydroxide dissolves more slowly in 2-propanol than in ethanol.

Use in Qualitative Tests. In certain qualitative tests for chromates, borates, and acetates, ethanol is used as a reagent or as a solvent for a reagent. In order to test the suitability of 2-propanol for this purpose the tests were carried out in duplicate, using ethanol in one case and 2-propanol in the other.

The test for chromates depends upon the reducing action of alcohol on sexivalent chromium to form green tervalent chromium. For this test 2-propanol was as satisfactory as ethanol, using the procedure recommended by Curtman (*3*).

Two tests for borates are given by Curtman. One is the common flame test which indicates the presence of borates by a green coloration imparted to the burning alcohol. When 2-propanol is used, a satisfactory coloration is not obtained because of the smokiness of the flame, which obscures the slight green color. The lack of color may also be due to the lower volatility of the isopropyl ester. The turmeric test described by the same author is successful with both ethanol and 2-propanol. However, the test is not as sensitive with the latter alcohol, no color being produced with a 0.01 per cent solution of borax, while ethanolic solutions of turmeric did produce a color at this concentration.

The acetate test as given by the U. S. Pharmacopeia (*22*) depends upon the formation of the acetic acid ester of the alcohol used. This test is not successful with 2-propanol, presumably because the alcohol is unstable in the presence of concentrated sulfuric acid (*20*).

Quantitative Uses

In the presentation of the experimental results for the quantitative determinations employing 2-propanol as a reagent the details of the procedures used are not included, because in most cases they are readily available in the literature. In general, the determinations were run in triplicate with each alcohol, six aliquot portions being taken from a solution of a salt of the constituent to be determined. In some cases the strength of the stock solution was determined by an analysis of a third set of triplicates, and in other cases the solution was prepared by direct weighing and dilution to definite volume of a twice recrystallized salt.

Table V. Solubility of Calcium, Barium, and Strontium Nitrates in Absolute Ethanol and 2-Propanol

(Grams of salt per 100 grams of solvent at 25° C.)

Salt	Solubility Ethanol	Solubility 2-Propanol
$Ba(NO_3)_2$	0.0020	0.0020
	0.0016	0.0016
$Sr(NO_3)_2$	0.0086	0.0023
	0.0062	0.0014
$Ca(NO_3)_2$[a]	....	2.65
	85.40	2.69

[a] Values uncertain, presumably because of compound formation. See D'Ans and Siegler, *Z. physik. chem.*, 82, 35 (1913).

Table VI. Determination of Calcium and Strontium as Sulfates

(Alcohol used to decrease solubility of precipitates)

Constituent Determined	Amount Present	Ethanol Found	2-Propanol Found
	Gram	*Gram*	*Gram*
Sr	0.4158	0.4062	0.4045
		0.4058	0.4047
		0.4057	0.4050
		Av. 0.4059	Av. 0.4047
Sr	0.1023	0.1021	0.1031
		0.1029	0.1031
			0.1023
		Av. 0.1025	Av. 0.1028
Ca	0.06577	0.06546	0.06547
		0.06564	0.06555
		0.06558	0.06552
		Av. 0.0656	Av. 0.0655
Ca	0.0995	0.09960	0.09969
		0.09969	0.09960
		0.09958	0.09975
		Av. 0.0996	Av. 0.0997

Solubilities. When alcohol is used as a selective solvent in the separation of two or more constituents of a mixture the deciding factor in its application is the solubility of the material in the alcohol. If 2-propanol is to be substituted for ethanol in such procedures it is desirable to know something of the solvent properties of the former as compared with the latter.

In order to compare the variation of solubility in the two alcohols with temperature and concentration of alcohol, a number of solubility determinations were made.

Duplicate determinations were made by placing an excess of the dried salt in each of two glass tubes with a capacity of about 100 ml. The tubes were then nearly filled with alcohol and sealed. One of the tubes was placed in the thermostat immediately after being sealed off and the other was held at a temperature about 10° above that of the thermostat for about an hour and then transferred to the thermostat. The tubes were held in a rack which was arranged in such a manner that it could be rotated, turning the tubes end over end. The tubes were rotated for a period of 12 hours.

At the end of 12 hours the rotation was stopped and the excess salt was allowed to settle to the bottom. The tip of the tube was then broken off and the solution drawn off into a weighing bottle through a tube containing a sintered glass filtering disk. The weighing bottle was stoppered and weighed after standing in the balance case for 15 minutes. The alcohol was then evaporated and the residue dried at 110° C., cooled, and weighed. The results for sodium and potassium chlorides are shown in Tables III and IV.

The solubilities of calcium, barium, and strontium nitrates are shown in Table V. The procedure used for these salts was the same as that for the sodium and potassium chlorides.

To Make Separations. In making separations of metallic ions the samples were prepared by making a stock solution of each of the constituents, standardizing each solution, and taking 25 ml. of each solution for a sample.

The separation of calcium from barium by extraction of the calcium nitrate with a mixture of absolute alcohol and ether was carried out according to the procedure given by Hillebrand and Lundell (*11*). The mixture of nitrates used contained 0.05018 gram of calcium oxide and 0.5015 gram of barium oxide. The calcium was not determined after the extraction.

Separation with ethanol:
BaO: 0.0486; 0.0485; 0.0488; Av. 0.0486
Separation with 2-propanol:
BaO: 0.0487; 0.0490; 0.0491; Av. 0.0489

Table VII. Alcohols as Washing Media for Precipitates

Constituent Determined	Amount Present	Ethanol Found		2-Propanol Found	
	Gram	%	*Gram*	%	*Gram*
Pb as $PbSO_4$ (*14*, p. 523)	0.2051	95	0.2046	91	0.2044
			0.2044		0.2046
			0.2044		0.2046
			Av. 0.2044		Av. 0.2045
Mg as $MgNH_4PO_4 \cdot 6H_2O$ (*6*, pp. 222, 224)	0.02433	95	0.02426	91	0.02423
			0.02425		0.02425
			0.02424		0.02424
			Av. 0.02425		Av. 0.02424
CNS as AgCNS (*21*, p. 303)	0.07686	95	0.07632	91	0.07667
			0.07654		0.07663
			0.07667		0.07667
			Av. 0.0765		Av. 0.07666
Cr as $BaCrO_4$ (*21*, pp. 106–7)	0.02689	50	0.02662	50	0.02666
			0.02660		0.02670
			0.02656		Av 0.02668
			Av. 0.02659		
Cd as $Cd_2P_2O_7$ (*21*, p. 192)	0.1028	60	0.1077	60	0.1066
			0.1074		0.1065
			0.1069		0.1071
			Av. 0.1073		Av. 0.1067
Cu as CuCNS (*21*, p. 187)	0.1730	20	0.1724	20	0.1719
			0.1717		0.1722
			0.1721		0.1721
			Av. 0.1721		Av. 0.1721
Cd as $CdNH_4PO_4 \cdot H_2O$ (*4*, pp. 401–15)	0.1079	95	0.1076	91	0.1077
			0.1078		0.1082
			0.1076		0.1079
			Av. 0.1077		Av. 0.1079
Na as sodium zinc uranyl acetate (*1*, p. 1625)	0.00200	95[a]	0.00197	91[a]	0.00195
			0.00200		0.00196
			0.00196		0.00192
			Av. 0.00198		Av. 0.00194
Na as sodium magnesium uranyl acetate (*2*, p. 1664)	0.0100	95	0.0100	91	0.00987
			0.0101		0.00988
			0.0100		0.00988
			Av. 0.0100		Av. 0.00988
				91[a]	0.00987
					0.00991
					0.00995
					Av. 0.00991
Zn as $ZnNH_4PO_4$ (*21*, p. 142)	0.1168	50	0.1169	50	0.1168
			0.1166		0.1165
			0.1171		0.1169
			Av. 0.1169		Av. 0.1167
Zn as $ZnNH_4PO_4$ (*4*, p. 401–15)	0.1123	65	0.1121	65	0.1122
		&	0.1120	&	0.1119
		95	0.1121	91	0.1119
			Av. 0.1121		Av. 0.1120
Cu as copper pyridinothiocyanate (*19*, p. 185)	0.0602	70	0.06037	70	0.06017
		&	0.05994	&	0.06060
		95	0.05981	91	0.06062
			Av. 0.0600		Av. 0.0605
Ca as $CaC_2O_4 \cdot H_2O$ (*5*, p. 352)	0.1343	95	0.1354	91	0.1358
			0.1354		0.1359
			0.1356		0.1362
			Av. 0.1355		Av. 0.1360
Ba as $BaSO_4$ (*5*, p. 352)	0.1408	95	0.1414	91	0.1415
			0.1405		0.1408
			0.1411		0.1414
			Av. 0.1410		Av. 0.1412
Ni as nickel dimethyl glyoxime (*5*, p. 352)	0.0552	95	0.05535	91	0.05515
			0.05523		0.05535
			0.05537		0.05525
			Av. 0.0553		Av. 0.0553
Cl as AgCl (*5*, p. 352)	0.0998	95	0.1000	91	0.0995
			0.0997		0.1000
			0.1000		0.1001
			Av. 0.0999		Av. 0.0999

[a] Alcohol used for washing was saturated with the precipitate.

Calcium was separated from magnesium by precipitation according to the method given by Hillebrand and Lundell (*11*). The following amounts were recovered from a sample which contained 0.0102 gram of calcium oxide and 0.02383 gram of magnesium oxide:

Separation with ethanol:
CaO: 0.0108; 0.0101; Av. 0.0104
MgO: 0.02388; 0.02327; Av. 0.0236
Separation with 2-propanol:
CaO: 0.0100; 0.0092; 0.0103; Av. 0.0098
MgO: 0.02390; 0.02401; 0.02416; Av. 0.0240

Potassium and sodium chlorides were separated from magnesium chloride according to the procedure given by the same authors (*11*). The sample contained 0.07975 gram of combined alkali chlorides (1 to 1) and 0.0953 gram of magnesium oxide. Because the evaporation of the solution containing the sodium and potassium chlorides left a residue of organic matter which could not readily be removed only the magnesium was determined after separation.

Separation with ethanol:
MgO: 0.0954; 0.0941; 0.0948; Av. 0.0948
Separation with 2-propanol:
MgO: 0.0918; 0.09261; 0.0923; Av. 0.0922

A repetition of this procedure with 0.1129 gram of magnesium oxide in the presence of 0.0843 gram of sodium and potassium chlorides (7 to 10) gave the following results:

Separation with ethanol:
MgO: 0.1098; 0.1107; 0.1115; Av. 0.1107
Separation with 2-propanol:
MgO: 0.1121; 0.1125; 0.1131; Av. 0.1126

In a separation of the same elements according to the Palkin method (*16*) using 0.0843 gram of sodium and potassium chlorides (7 to 10) in the presence of 0.1129 gram of magnesium oxide the following results were obtained:

Separation with ethanol:
NaCl and KCl: 0.0884; 0.0881; 0.0886; Av. 0.0884
Separation with 2-propanol:
NaCl and KCl: 0.0846; 0.0843; Av. 0.0844

The magnesium was not determined in this separation. The alkali chlorides are precipitated in this determination by the addition of absolute alcohol and ether. A double precipitation is necessary with ethanol, but with 2-propanol a single precipitation completely separated the sodium and potassium chlorides.

To Decrease Solubilities. In some instances ethanol is used to decrease the solubility of precipitates which are too soluble to be precipitated from aqueous solution. Examples of this use are the determinations of strontium and calcium as sulfates. The procedure for calcium is given by Treadwell and Hall (*21*) and that for strontium by Mahin (*14*). Typical results are shown in Table VI.

To Wash Precipitates. Alcohol is used quite frequently for washing precipitates, generally for one of two reasons: the precipitate is less soluble in alcohol than in some other medium; or, there is some advantage in using a low-boiling washing medium either to obtain more rapid drying or to make it possible to dry at relatively low temperatures those precipitates which decompose at the ordinary drying temperatures.

Table VII contains the results of experiments to compare the suitability of ethanol and 2-propanol as washing media.

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Colorimetric Standards for Silica

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One of the methods recommended for the colorimetric determination of small amounts of dissolved silica depends upon the formation of a yellow heteropoly compound, molybdisilicic acid, by the reaction of ammonium molybdate and the silica in the presence of a mineral acid. Since the usefulness of this procedure for routine work is limited by the instability of solutions of silica and of the yellow color, permanent standards have been proposed by various individuals.

The purpose of the present work was to study, by means of a spectrophotometer, these or other possible standards to determine the system most nearly meeting the requirements of an ideal colorimetric standard. The latter, in addition to being permanent and reproducible, should transmit the same amount of light at each wave length as the substance which it is to match, if the hues are to be identical under all conditions.

In the original recommendation of the method in 1898, Jolles and Neurath (*5*) used potassium molybdate and nitric acid as reagents and known solutions of silica for comparison. Winkler (*14*) modified the method by substituting hydrochloric for nitric acid and by introducing aqueous solutions of potassium chromate for standards. A solution containing 0.53 gram per liter of this salt was stated to be equivalent in color to 100 p. p. m. of silica. Dienert and Wandenbulcke (*3*) used ammonium molybdate and sulfuric acid and, as a standard, an aqueous solution of picric acid containing 35.9 mg. per liter, equivalent to 50 p. p. m. of silica. Atkins (*2*) employed the same concentration of this standard, but Thresh and Beale (*12*) recommended 40 mg. Believing the picric acid used by previous workers contained moisture, King and Lucas (*7*) proposed 25.6 mg. of dried material as equivalent to 50 p. p. m. of silica. Thompson and Houlton (*11*) recently reported using picric acid standards. Steffens (*9*) thought the reddish yellow hue of the potassium chromate solution did not match the greenish yellow obtained with silica and ammonium molybdate, an observation confirmed by the work of Liebknecht, Gerb, and Bauer (*8*). Winkler's potassium chromate standards were adopted, however, by the American Public Health Association in 1933 (*1*).

Experimental Work

Preparation of Materials. Several types of silica solutions were used, two being made from different samples of c. p. sodium silicate and a considerable number from definite amounts of c. p. silica or acid-washed sea sand fused with sodium carbonate. The former were standardized at intervals gravimetrically and kept in Pyrex glass bottles. The latter were discarded if more than 48 hours old. These solutions contained 500 to 5000 p. p. m. of silica and were diluted for use.

Picric acid recrystallized from benzene was used to prepare solutions of the concentrations recommended by King and Lucas and by Dienert and Wandenbulcke. Borax and potassium chromate were recrystallized. All the water used came from a special still built entirely of tin and Pyrex glass. Both c. p. ammonium molybdate and that prepared from molybdic acid and redistilled ammonium hydroxide were used.

Apparatus. A Keuffel and Esser spectrophotometer served for obtaining transmission data, using 20-cm. cells. In contrast to the usual practice with this instrument, the transmissions of the solution and solvent were determined separately and the transmittancy calculated from these values. Ordinary visual comparisons were made both in tall-form Nessler tubes with plane glass ends and in a Duboscq-type colorimeter by the substitution method (*15*).

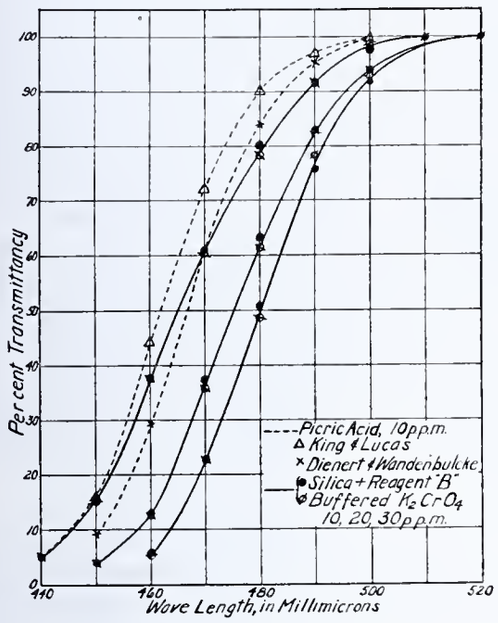

Figure 1. Spectral Transmission Curves for Picric Acid Standards, Buffered Potassium Chromate Standards, and Silica Solutions with Reagent B

A photoelectric colorimeter similar to that described by Story and Kalichevsky (*10*) proved to be both sensitive and rapid in determining the effect of different factors on the intensity and stability of the yellow color. Blue glass filters isolated the part of the spectrum in which yellow solutions absorb light. Galvanometer deflections were noted for a constant thickness of solution.

Color Reaction. The selection of satisfactory permanent standards presupposes a knowledge and control of the conditions likely to affect the stability and reproducibility of the color produced with the silica in the unknown. After surveying the work of others upon this point, different variations in reagents, concentrations, and other conditions were tried. On the basis of the results obtained, two reagents were selected for use in the study of permanent standards. For the first, now recommended by the American Public Health Association (A. P. H. A. Reagent), one adds to 100 ml. of unknown 10 ml. of a solution containing 200 ml. of hydrochloric acid (1 to 1), 30 grams of ammonium molybdate, and 400 ml. of water. For the second (Reagent B), adapted from Dienert and Wandenbulcke's recommendation, one adds to 100 ml. of unknown 4 ml. of 10 per cent ammonium molybdate and 1 ml. of 20 per cent sulfuric acid.

There seems to be an optimum amount of acid required for the full development of the yellow color. Either too much or too little gives decreased intensities, presumably from an effect on the heteropoly complex. The acidity of the A. P. H. A. Reagent is near the maximum. Acidities somewhat less gave just as satisfactory colors with this reagent.

Use of each of the two reagents mentioned gave a reproducible series of results, complete development of color occurring within 5 minutes and no fading within 30 minutes. However, the A. P. H. A. Reagent gave approximately 10 per cent greater intensity of color than Reagent B. The color developed with these reagents is proportional to the silica, at least as high as 75 p. p. m. Transmittancy data were determined for each reagent for concentrations of silica of 10, 20, and 30 p. p. m., thus providing curves with which to compare those of possible permanent standards.

Picric Acid Standards. In Figure 1 are shown spectral transmission curves for solutions of picric acid equivalent to 10 p. p. m., the concentrations being those recommended by King and Lucas and by Dienert and Wandenbulcke. A comparison of these curves with those for silica of the same concentration with Reagent B shows that the standards do not transmit the same amount of light at most wave lengths as the silica solution. The curve for Dienert and Wandenbulcke's solution of acid is fairly close to that for the corresponding silica solution, but no change of concentration would bring together the curves for the standard and the unknown. Similar data were obtained for solutions of picric acid designed to match other concentrations of silica, but only the curves for the latter solutions are shown. Although picric acid solutions show reasonable stability and conformity to Beer's law, the curves show that the system cannot be as satisfactory as one meeting more nearly the criteria of an ideal standard. In Nessler tubes differences are apparent between either of the two concentrations of standard and the corresponding silica solution.

Potassium Chromate Standards. In agreement with the report of Steffens, differences in hue could be noted easily in Nessler tubes between silica and potassium chromate solutions. The observations of Viterbi and Krausz (*13*), Hantzsch and Clark (*4*), and Jorgensen (*6*) concerning the

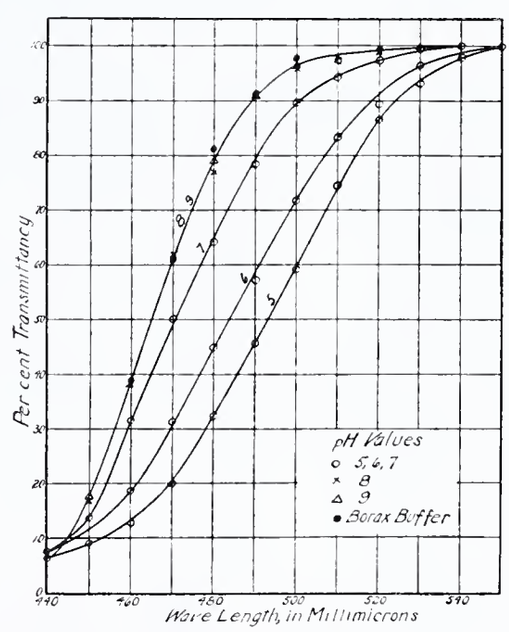

Figure 2. Spectral Transmission Curves for Solution of Potassium Chromate at Different pH Values

variability of the chromate-dichromate equilibrium in solutions of potassium chromate gave a possible clue to the objection to this system as a standard. To determine the effect of hydrogen-ion concentration on the hue, a series of solutions equivalent to 10 p. p. m. of silica was prepared in buffer solutions to give pH values of 5, 6, 7, 8, and 9. From the curves in Figure 2 showing their transmittancy data, it is evident that a decrease in hydrogen-ion concentration caused a decided change in hue to a pH value of about 8, beyond which little change occurred. A fresh, unbuffered solution gave a curve indicating a pH value between 6 and 7. It is evident that such systems may be affected by absorption of carbon dioxide or alkali from the glass.

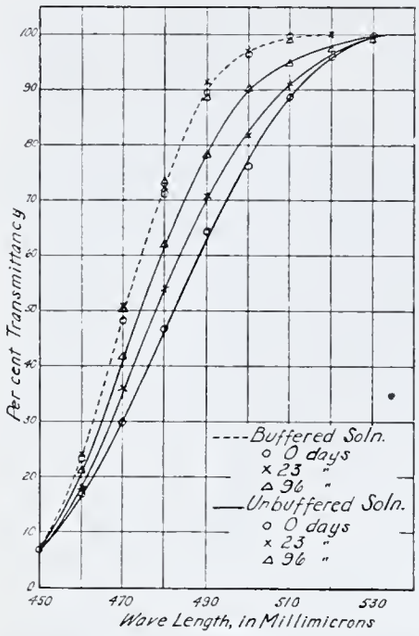

FIGURE 3. SPECTRAL TRANSMISSION CURVES FOR BUFFERED AND UNBUFFERED SOLUTION OF POTASSIUM CHROMATE AT DIFFERENT PERIODS OF TIME

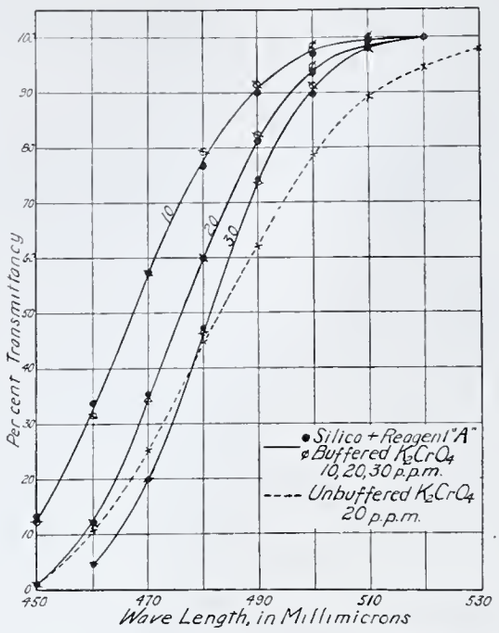

FIGURE 4. SPECTRAL TRANSMISSION CURVES FOR UNBUFFERED POTASSIUM CHROMATE SOLUTION AND FOR BUFFERED POTASSIUM CHROMATE STANDARDS AND SILICA WITH A. P. H. A. REAGENT

In view of these facts, an unbuffered solution equivalent to 15 p. p. m. of silica was kept in a flint glass bottle for 3 months. The transmittancy data, shown in Figure 3, show a gradual shift of the curves with time toward the position for an alkaline solution. No appreciable change was noted after the seventy-third day.

The similarity of the curves in the alkaline region to those for silica suggested the use of buffered solutions of potassium chromate as standards. Accordingly, enough of a 1 per cent solution of sodium tetraborate was used in diluting the standards to make the final solution 50 per cent by volume of the buffering reagent. The stability of such a buffered system is indicated by the broken line curve in Figure 3. Measurements with a colorimeter disclosed close conformity to Beer's law for the buffered solutions at least as far as 100 p. p. m. This was checked for the range 10 to 50 p. p. m. with data from a recording photoelectric spectrophotometer. An alkaline buffer makes practical the use of equivalent amounts of potassium dichromate, which, as a primary standard, may be more readily available than the chromate.

TABLE I. COLORIMETRIC STANDARDS FOR DETERMINATION OF SILICA

Potassium Chromate[a]	Silica[b]	Potassium Chromate	Silica
Ml.	*P. p. m.*	*Ml.*	*P. p. m.*
0.0	0	8.0	16
1.0	2	9.0	18
2.0	4	10.0	20
3.0	6	11.0	22
4.0	8	12.0	24
5.0	10	13.0	26
6.0	12	14.0	28
7.0	14	15.0	30

[a] 0.63 gram of potassium chromate per liter. The volumes specified are to be diluted with 25 ml. of a 1 per cent solution of borax and enough water to make a total of 55 ml.

[b] When 50 ml. of sample are used, together with 5 ml. of reagent, as recommended in the A. P. H. A. method.

As a buffered solution of potassium chromate transmits more light than one unbuffered, it is necessary to use a concentration higher than that recommended by the A. P. H. A. method to give a color equal to a given amount of silica. In order to determine the amount to use, measurements were made with three different colorimeters, Nessler tubes, and the spectrophotometer, covering a period of several months and using various solutions of silica and ammonium molybdate. To be equivalent to a silica solution of 100 p. p. m., the amounts recommended are 0.63 and 0.58 gram per liter for the A. P. H. A. Reagent and Reagent B, respectively. One milliliter of this stock solution, diluted with 50 ml. of a 1 per cent solution of sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$, and enough water to make a total of 100 ml., is equivalent to 1 p. p. m. of silica. The details of diluting the standards depend upon the total volume of the molybdate reagent, the acid, and the sample, but in any case the volume of the standard and unknown should be the same.

The curves in Figures 1 and 4 show for three concentrations the good agreement of the data for these standards and for silica solutions treated with one of the two different reagents. In view of these results, the buffered solution of potassium chromate was considered so much better than picric acid that no further work was done upon it.

For use in determining silica in water according to the A. P. H. A. method, the values given in Table I are recommended as a substitute for those on page 67 of the 1933 edition of "Standard Methods of Water Analysis." A careful gravimetric determination of the silica in a well water checked the value obtained colorimetrically with this table.

SUMMARY

A comparison of silica solutions and standards by means of visual and photoelectric colorimeters, Nessler tubes, and a spectrophotometer would seem to justify the following conclusions:

1. Either the A. P. H. A. reagent or an adaptation of that of Dienert and Wandenbulcke is generally satisfactory for producing the yellow color with silica.
2. Solutions of picric acid or unbuffered potassium chromate are not considered as meeting satisfactorily the requirements of a permanent standard.
3. A solution of potassium chromate suitably buffered, as with borax, provides a standard possessing none of the disadvantages of those now recommended.
4. To use the latter solution a new table is recommended.

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Identification of Amines as 2,4-Dinitrobenzoates

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THE amine salts of sulfonic (*3*, *6*) and carboxylic (*1*) acids have been recommended as derivatives for the identification of amines. Such salts appear to be of sufficient stability, provided the strength of the acid employed is great enough. The success met with 3,5-dinitrobenzoic acid with an ionization constant of 1.55×10^{-3} (*4*) suggested the use of 2,4-dinitrobenzoic acid in which this constant has increased to 3.5×10^{-2} (*4*).

In the main, there is little to choose between these two dinitrobenzoic acids as reagents for amine identification. Both combine with a wide variety of aliphatic and aromatic amines to such an extent that isolation of the salts in a pure form is usually readily accomplished. The results with the 2,4 acid, as shown in Table I, include for comparison the melting points of the corresponding salts with the 3,5 acid. None of these compounds, with the exception of those of ammonia (*5*) and pyridine (*7*), has been found in the literature.

Experimental

Preparation of 2,4-Dinitrobenzoic Acid. The 2,4-dinitrobenzoic acid was prepared by Curtius' method (*2*) as modified by E. L. Lafferty in this laboratory. The details are as follows:

With mechanical stirring 100 grams of 2,4-dinitrotoluene, Eastman's highest grade, melting point 69.5° to 70.5° C., were dissolved in 600 cc. of concentrated sulfuric acid at 50° C. A chromic acid solution was prepared by dissolving 158 grams of powdered U. S. P. potassium dichromate in 200 cc. of water, and then adding cautiously 100 cc. of concentrated sulfuric acid. The chromic acid solution, kept near boiling to prevent solidification, was added dropwise through a separatory funnel to the 2,4-dinitrotoluene solution, which was being vigorously stirred in a round-bottomed flask placed in an ice bath. During this addition the temperature of the reacting mixture was not allowed to exceed 65° (60° to 65° C. appeared to be the most favorable range). When the addition was complete, stirring was continued for 15 minutes and the mixture was allowed to cool to room temperature, after which ice was added in a quantity sufficient to double the volume. When the ice had melted, the remaining solid was removed by filtration.

The filtrate, since it contained a small amount of the dinitrobenzoic acid, was thoroughly extracted with about 300 cc. of ether. After evaporating off the ether from the upper layer, the solid thus obtained was added to the original residue. In order to separate any unchanged dinitrotoluene, a strong solution of sodium bicarbonate was added to the combined residues until the solution became basic to litmus. The solid dinitrotoluene was then removed by filtration, after which an excess of concentrated hydrochloric acid was added to the filtrate to precipitate out the free 2,4-dinitrobenzoic acid. This acid, after being filtered and washed thoroughly with a cold dilute solution of hydrochloric acid, was redissolved in a saturated solution of sodium bicarbonate, an equal volume of water was added, and the solution thus obtained was made slightly acid with concentrated hydrochloric acid.

The precipitated acid, when filtered, washed with ice water, and dried on filter paper in the air, weighed about 45 grams (40 per cent of the theoretical amount). It had a yellow color and melted at 179° C. The color of the product

Table I. 2,4-Dinitrobenzoates of Amines

Amine	Recrystallized	Color	Molar Ratio	Neutralization Equivalent Calcd.	Neutralization Equivalent Found	Nitrogen Calcd.	Nitrogen Found	Melting Point Obs. °C.	Melting Point Cor. °C.	Melting Point of 3,5-Dinitrobenzoate Cor. °C.
Aniline	0[a,b]	Pink	1:1	305	314	13.77	13.83	157.8–159.4	160.4–162.0	134.7
o-Toluidine	1	White	1:1	319	316	13.17	13.21	189.5–191.2	193.2–194.9	134.9
m-Toluidine	0[a,b]	Yellow	1:1	319	312	13.17	13.18	142.0–143.6	144.5–146.1	139.0–144.0
p-Toluidine	1	Red	1:1	319	316	13.17	13.04	158.2–159.6	160.8–162.2	145.0–147.4
4-Amino-1,3-dimethylbenzene	1	Yellow	1:1	333	337	12.61	12.52	172.0–172.4	175.1–175.5	169.6–170.4
o-Chloroaniline	1	Yellow	1:1	340	335	12.38	12.41	135.6–136.4	137.9–138.7	152.7
m-Chloroaniline	1	Yellow	1:1	340	337	12.38	12.42	139.6–140.4	142.0–142.8	121.8
p-Chloroaniline	1	Yellow	1:1	340	336	12.38	12.40	161.8–162.4	164.5–165.1	133.0
p-Bromoaniline	1	Brown	1:1	384	383	10.94	10.91	179.0–179.6	182.6–183.2	126.9
o-Nitroaniline	No compound isolated									.....
m-Nitroaniline	1	Yellow	1:1	350	352	16.00	16.02	131.2–131.6	133.0–133.4	112.0–114.4
p-Nitroaniline	0[b]	Yellow	1:1	350	358	16.00	16.01	116.0–116.9	117.3–118.2	128.6
p-Aminophenol	1	Brown	1:1	321	317	13.09	13.03	200.0–200.2	204.3–204.5	178.2–178.8
o-Aminobenzoic acid	1	Yellow	1:1	175	167	12.04	12.04	148.0–149.0	150.5–151.5	205.2–205.6
m-Aminobenzoic acid	1	White	1:1	175	177	12.04	11.93	184.5–186.0	188.1–189.6	167.0–172.2
p-Aminobenzoic acid	1	Yellow	1:1	175	171	12.04	12.18	165.4–166.0	168.3–168.9	196.7
Methylaniline	0[a,b]	Brown	1:1	319	310	13.17	13.07	101.6–102.8	102.6–103.8	121.8
Dimethylaniline	0[a,b]	Yellow	2:1	273	265	12.85	12.78	101.4–103.0	102.4–104.0	114.8–115.6
Benzylaniline	1	Yellow	1:1	395	385	10.63	10.77	120.0–120.8	121.4–122.2	133.0
Dibenzylaniline	No compound isolated									.....
Acetanilide	2[c]	White	1:1	347	350	12.11	12.09	87.4–90.4	87.9–90.9	129.1–130.1
Diphenylamine	0[d]	Gray	1:1	381	378	11.02	10.99	[d]		.....
Triphenylamine	No compound isolated									.....
o-Phenylenediamine	1	Yellow	1:1	320	318	17.50	17.46	193.2–193.6	197.5–197.9	177.3
m-Phenylenediamine	1	Yellow	1:1	320	324	17.50	17.52	193.0–193.2	197.3–197.5	158.7
p-Phenylenediamine	1	Golden yellow	1:1	320	319	17.50	17.57	177.8–179.0	181.4–182.6[e]	177.3–178.0
α-Naphthylamine	1	Yellow	1:1	355	357	11.83	11.94	195.0–195.4	199.3–199.7	200.5
β-Naphthylamine	1	Yellow	1:1	355	355	11.83	11.98	177.8–178.2	181.4–181.8	156.5–157.2
Benzidine	1[f]	Red	2:1	304	306	13.82	13.81	225.8–227.0	231.8–233.0[e]	205.7
Pyridine	1	Brown	2:1	252	246	[g]	[g]	138.6–139.4	140.9–141.7	171.3
Quinoline	1	Brown	1:1	341	336	12.34	12.37	139.6–140.4	142.0–142.8	151.4–152.2
Ammonia	1	Yellow	1:1	229	233	18.34	18.30	213.4–215.4	218.5–220.5	246.7
Benzylamine	0[a]	Yellow	1:1	319	325	13.17	13.14	194.8–195.8	199.1–200.1	210.0
Diethylamine	0[a]	Yellow	1:1	285	281	14.74	14.74	145.0–146.6	147.5–149.1	163.4
Triethylamine	0[a]	Yellow	1:1	313	317	13.42	13.59	80.6–82.5	81.0–82.9	138.0–150.0
Urea	1[c]	Yellow	1:1	272	275	20.59	20.63	127.4–128.2	129.1–129.9	120.5
Acetamide	1	Yellow	1:1	271	264	15.49	15.52	109.8–110.8	111.1–112.1	93.9–103.9
Benzamide	1	Orange	1:1	333	328	12.62	12.52	116.8–117.8	118.1–119.1	138.6–140.4

[a] Purified by washing in ethyl alcohol as described in Experimental.
[b] Decomposition occurred on redissolving compound.
[c] Prepared in and recrystallized from a mixture of alcohol and water.
[d] Since this compound was extremely unstable, the melting point is of little significance.
[e] Compound turned dark below melting point.
[f] Prepared in and recrystallized from a mixture of alcohol and ether.
[g] Nitrogen could not be determined by the Kjeldahl method.

is determined to some extent by the rapidity with which the acid is precipitated from solution. Rapid precipitation from the acidified bicarbonate solution yielded some very red crystals, while slow cooling of a saturated neutral bicarbonate solution gave long colorless needles.

Preparation of Salts and Analyses. As a rule, to form the salts, 0.01 mole of each component was dissolved by heating in the least possible amount of absolute alcohol, after which the two solutions were poured together on a watch glass to crystallize. However, the compounds of aniline, *o*-toluidine, *m*-toluidine, methylaniline, dimethylaniline, benzylamine, diethylamine, and triethylamine were prepared by adding, in equimolecular amounts, the hot liquid amine to the very finely powdered acid. Although purification was usually accomplished by recrystallization from absolute alcohol (Table I), these latter-mentioned salts were purified almost entirely by pulverizing them in cold absolute alcohol, followed by filtration. The number of crystallizations necessary for purity in each case is indicated in the second column of Table I.

The melting points, neutralization equivalents, and nitrogen analyses were determined as described previously (*1*).

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Determination of Organic Halogens

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It has been reported by Jenkins, McCullough, and Booth (*5*) that the explosion method for organic halogen determination as outlined by Lemp and Broderson (*6*) produces consistently low results with ortho and para chlorinated diphenyls. Cook and Cook (*3*) also state that this method produces unsatisfactory results with halogenated diphenyls. Adams (*1*) and his co-workers have reported satisfactory results on halogenated diphenyl and diphenylbenzene compounds, using the bomb-explosion method.

The present investigation was undertaken to determine whether or not the substituted halogens of these compounds and others with which the author has experienced some difficulty could be completely converted to sodium halide when subjected to the sodium peroxide–sugar explosion. It has been the author's experience that certain variations introduced into the procedure for determination of organic halogens by the explosion method produce inconsistent and low results; however, the experience gained in this laboratory through many hundreds of analyses on organic halogens prompts the statement that this method is destined to be considered as generally applicable as the Dumas method for nitrogen. Contrasted with distillation methods and the Carius method it is extremely rapid and simple of operation, besides being as accurate as any reported macromethod for organic halogen determinations.

Procedure

The sample used should be such that the silver halide will weigh not more than 275 mg., as much larger samples are not completely oxidized. Add 12 grams or 1 scoop of sodium peroxide and 200 mg. of lactose, shake the whole thoroughly for about 45 seconds, and place in the hottest part of the Bunsen flame for about 45 seconds. This should be done behind a protective screen. Drop the bomb into cold water and wash with distilled water. Dissolve the fusion and remove the cup in the usual manner. Add 50 cc. of 1 to 1 nitric acid slowly, and remove the gas by stirring or, if desired, boiling in the case of chlorides. Filter through a fine grade of filter paper and wash completely. Add very slowly while stirring excess 0.1 *N* silver nitrate. Stir to coagulate and filter through a Gooch crucible. Wash the silver halide with 300 cc. of water, dry at 140° C. for 1 hour, cool on copper block for about 20 to 25 minutes, and weigh.

Potassium nitrate has been reported by Elek and Hill (*4*), Lemp and Broderson (*6*), and others as a necessary constituent of the explosion mixture and has been used to some extent in this laboratory. However, all results reported in this article and many others have been obtained without potassium nitrate, and it may be concluded that potassium nitrate is not a necessary constituent of the explosion mixture.

Table I is included to indicate the range of applicability and accuracy of the method.

Table I. Typical Results Obtained in Some Compounds Analyzed[a]

Substance	Halogen Calculated %	Halogen Obtained %
m-Chloronitrobenzene	22.50	22.45 22.45
2,5-Dichloronitrobenzene	36.88	36.96 36.86
1,2,4-Dichloroaniline	43.78	43.75 43.76
Hexachlorobenzene	74.71	74.56 74.71
m-Nitrobenzalchloride	34.43	34.43 34.43
m-Bromobenzoic acid	39.77	39.64 39.74
p-Chloroacetanilide	20.92	20.94 21.02
9,10-Dibromoanthracene	47.58	47.53 47.47
Chloroacetophenone	22.95	22.96 23.00
6-Chlorocoumarin	19.64	19.58 19.73
5,7-Dibromo-8-hydroxyquinoline	52.77	52.72 52.71
Trichlorobutyric acid	55.57	55.46 55.46
Propylene bromide	79.17	79.20 79.29
Iodopropionic acid	63.47	63.46 63.49
Chloroacetamide	37.92	37.96 37.95
Triphenylchloromethane	12.73	12.79 12.75

[a] Compounds were purified where necessary.

Discussion

Determination of Halogenated Diphenyls. A sample of the *o*- and *p*-chlorodiphenyl taken from the original stock was obtained from Jenkins, McCullough, and Booth (*5*). The results obtained on halogenated diphenyls and a substituted diphenylbenzene, together with those obtained by Huntress and reported by Jenkins, McCullough, and Booth (*5*), appear in Table II, and indicate that by means of the procedure here employed consistent and accurate results can be obtained on halogenated diphenyls. The sample of the substituted diphenylbenzene was provided by Roger Adams, University of Illinois.

Table II. Results Obtained on Halogenated Diphenyls

Substance	Halogen Calculated	Huntress'[a] Results	Halogen Found
	%	%	%
o-Chlorodiphenyl	18.81	18.81	18.78
		18.79	18.76
			18.75
			18.74
			18.72
p-Chlorodiphenyl	18.81	18.79	18.86
		18.90	18.85
		18.86	18.74
			18.80
			18.75
p-Bromodiphenyl	34.30	...	34.34
		...	34.37
4,4-Dibromodiphenyl sulfone	42.63	...	42.65
			42.69
$C_{18}H_2Br_4(CH_3)_6(OH)_2$ (a brominated diphenylbenzene)	48.30	...	48.18
			48.21

[a] Carius method used.

Effect of Overheating Bomb Cup. In the procedure outlined by Lemp and Broderson (*6*) ignition is effected in the hottest part of the Bunsen flame, the heating being continued until the cup is red for at least one-fourth of its length. With certain organic bromine compounds when the stainless steel cup is used low results are obtained by so heating unless a suitable reducing reagent is employed. This was not observed when the nickel cup described by the author (*2*) was used, even though heating was continued until the gasket melted and flowed down the walls of the bomb.

The comparative results obtained using nickel and steel cups are illustrated in Table III. The explosion usually takes place about 20 to 35 seconds after the flame is applied to the bomb, so that further heating is unnecessary and rapidly depletes the life of the cup.

Table III. Effect of Overheating Nickel and Steel Cups

Substance	Time of Heating	Halogen: Calculated	Halogen: Steel cup	Halogen: Nickel cup
	Min.	%	%	%
Bromocamphor	0.5–0.75	34.59	34.50	34.58
	1	...	34.48	34.55
			34.41	34.57
			34.41	...
	2	...	33.50	34.58
			31.30	34.45
			32.33	34.52
	3	...	...	34.52
			...	34.49
Bromodiphenyl[a]	0.5–0.75	34.30	34.81	34.89
	2	...	33.91	34.84
Dibromobenzene	2	67.76	67.56	67.81
2,4-Dinitrochlorobenzene	0.5–0.75	17.51	...	17.51
	2	...	17.53	...

[a] This sample of bromodiphenyl was not purified.

Overheating either steel or nickel cups containing the chlorinated organic compounds did not appear to affect the result. When heating was continued for only 35 to 45 seconds, using either the nickel or steel cups, reducing reagents were in no case found necessary with either bromine or chlorine compounds.

Effect of Delayed Explosion. In most cases the effect of delay in exploding becomes important only after an interval of some hours and seems to affect only volatile compounds. With two compounds low results were obtained after a delay of 15 to 20 minutes. The amount of loss is illustrated in Table IV and, in some cases at least, does not appear to be due to leakage during the interval of rest.

Determination of Blanks. A great deal of the difficulty experienced in obtaining consistently accurate results may be traced to incorrect blanks. The crucible must be carefully prepared. A suitable method is to macerate a thin layer of asbestos with a fine stream of water, continuing until the filtered water shows no trace of suspended asbestos. The asbestos is then tapped down with the stirring rod. A fine grade of filter paper similar to Whatman's No. 32 must be used for the first filtration. Too rapid filtering requires much wash water to eliminate the last traces of sodium halide. No appreciable opalescence should appear in the wash water after filtering through the Gooch crucible. Coagulation is aided somewhat by addition of alcohol to the silver nitrate solution. Stirring the solution is sufficient to coagulate the silver halide and boiling is not necessary.

Table IV. Effect of Time Interval between Shaking Mixture and Explosion

Substance	Halogen: Immediate explosion	Halogen: After 15 to 20 minutes	Halogen: Over 15 hours	Halogen: Calculated
	%	%	%	%
p-Dichlorobenzene	48.20	47.69	47.77	48.25
			47.45	
			47.71	
m-Dichlorobenzene	48.29	47.92	46.78	48.25
	48.39	48.04		
Bromobenzene	50.91	50.94	49.64	50.91
	50.89	50.94		
Chlorotoluene	28.16	28.02	27.55	28.02
	28.00	28.11		
Chloroform	89.00	88.67	69.55	89.11
	89.13	89.21		
Dibromobenzene	67.66	...	67.64	67.76
	67.76	...		

Determination of Halogen in Compounds Which Sublime. The author has experienced some difficulty with compounds which sublime. For instance, with dibromoanthracene it was observed that the yellow compound remained on the cover of the cup and the results were often inconsistent and low. This was overcome by covering with a layer of sodium peroxide about 1 cm. deep after mixing the explosion mixture. The results obtained are given in Table I.

Influence of Melting Point. An intimate mixture of compound and explosion mixture apparently becomes essential only in the case of those substances with high melting points. Organic halogenated compounds with low melting points—i. e., up to about 90° C.—do not require a fine state of division. Liquids were weighed out in a glass bulb or tube. A thin glass rod sealed to the neck serves as a handle in filling, and should be broken off before placing the tube in the bomb cup. It is essential that the wall of the bulb be extremely thin.

Summary

The determination of substituted halogens in diphenyl and diphenylbenzene compounds by means of the sodium peroxide–sugar explosion has been accomplished.

Continued heating of the steel cup after the explosion produces low halogen results with some bromine compounds, while overheating the nickel cup does not affect results.

Addition of supplementary oxidizing substances to the sodium peroxide–sugar explosion mixture is not necessary.

The results obtained on chloroform indicate that the method is adapted to volatile liquids, although results may be low if the explosion is delayed.

Acknowledgment

The author is indebted to J. Russell for checking results of analysis.

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Determination of Total Reducing Sugars, Dextrose, and Levulose in Raw Cane Sugars

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In a paper published some time ago (*7*) the importance of determining dextrose and levulose in cane products was pointed out, and various ways in which this might be accomplished were discussed. It was concluded that Nijns's method (*6*) of estimating levulose by selective copper reduction promised to be useful for the purpose. It was also found that contrary to Nijns's statement, dextrose has a distinct reducing effect on the copper carbonate reagent, and that large quantities of sucrose reduce it measurably, especially in the presence of reducing sugars. Jackson (*3*) also found this to be true for a copper carbonate solution similar to Nijns's, but containing 25.3 instead of 15 grams of copper sulfate per liter. The method has been further studied by Jackson and Mathews (*4*), and their modification has been adopted by the Association of Official Agricultural Chemists (*1*). Because of the reducing effect of dextrose on the copper carbonate reagent, the determination of levulose in mixtures with other sugars requires a determination of total reducing sugars also. The tables given by Jackson and Mathews for this purpose are not directly applicable to the analysis of raw sugars.

Since raw sugars contain large quantities of sucrose with small quantities of dextrose and levulose, a correction for the reducing effect of the sucrose must be applied to the result of the copper carbonate reduction as well as to that of the total reducing sugar determination. While the first of these corrections is known from the work of Jackson and Mathews, the usual tables for reducing sugars in the presence of large quantities of sucrose consider only invert sugar, but not dextrose and levulose in varying proportions. It was therefore necessary to establish such a table. Following the example of Jackson and Mathews, the Lane and Eynon volumetric method (*5*) was chosen because it is more practical for routine work than the gravimetric procedures and is rapidly gaining ground in the cane-sugar industry. The Lane and Eynon tables have been extended so as to include columns of factors for levulose and for dextrose in varying proportions, in the presence of large quantities of sucrose, and for 10 ml. of Soxhlet solution.

The procedure prescribed by Lane and Eynon was followed in every detail, several series of analyses being run with solutions containing 10 and 25 grams, respectively, of sucrose in 100 ml., plus dextrose alone, levulose alone, and invert sugar, ranging in quantity from 90 to 300 mg. of each. The solutions were titrated against 10 ml. of Soxhlet solution. The results were plotted, interpolated, and the final values are shown in Table I.

The factors for invert sugar are generally a little higher than those given by Lane and Eynon. This is no doubt due to small differences in manipulation, and each analyst should check these values under his own individual conditions, or construct his own tables of factors.

A few check analyses are given in Table II.

In confirmation of a statement made by Lane and Eynon, that in the presence of a large excess of sucrose small variations in the details of the procedure have a much greater

Table I. Lane and Eynon Factors for Mixtures of Levulose and Dextrose

(10 ml. of Soxhlet solution)

A. In presence of 10 grams of sucrose in 100 ml

Titer	100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L	0 D 100 L
15	46.1	46.3	46.5	46.6	46.8	47.0	47.2	47.4	47.7	47.9	48.1
16	46.0	46.2	46.4	46.5	46.7	46.9	47.1	47.3	47.6	47.8	48.0
17	46.0	46.2	46.4	46.5	46.7	46.9	47.1	47.3	47.5	47.7	47.9
18	45.9	46.1	46.3	46.4	46.6	46.8	47.0	47.2	47.5	47.7	47.9
19	45.9	46.1	46.3	46.4	46.6	46.8	47.0	47.2	47.4	47.6	47.8
20	45.8	46.0	46.2	46.3	46.5	46.7	46.9	47.1	47.3	47.5	47.7
21	45.7	45.9	46.1	46.2	46.4	46.6	46.8	47.0	47.2	47.4	47.6
22	45.7	45.9	46.0	46.1	46.3	46.5	46.7	46.9	47.1	47.3	47.5
23	45.6	45.8	46.0	46.1	46.3	46.5	46.7	46.9	47.1	47.3	47.5
24	45.6	45.8	45.9	46.0	46.2	46.4	46.6	46.8	47.0	47.2	47.4
25	45.5	45.7	45.8	45.9	46.1	46.3	46.5	46.7	46.9	47.1	47.3
26	45.4	45.6	45.7	45.9	46.0	46.2	46.4	46.6	46.8	47.0	47.2
27	45.4	45.6	45.7	45.8	46.0	46.2	46.4	46.6	46.7	46.9	47.1
28	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.5	46.7	46.9	47.1
29	45.3	45.5	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8	47.0
30	45.2	45.4	45.5	45.7	45.8	46.0	46.2	46.4	46.5	46.7	46.9
31	45.2	45.4	45.5	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8
32	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8
33	45.1	45.3	45.4	45.5	45.6	45.8	46.0	46.2	46.3	46.5	46.7
34	45.0	45.2	45.3	45.5	45.6	45.8	46.0	46.2	46.3	46.5	46.7
35	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.2	46.4	46.6
36	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.2	46.4	46.6
37	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.0	46.2	46.4	46.5
38	44.9	45.0	45.2	45.3	45.5	45.6	45.8	46.0	46.1	46.3	46.5
39	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4
40	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4
41	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4
42	44.9	45.0	45.2	45.3	45.5	45.6	45.7	45.9	46.0	46.2	46.3
43	44.8	44.9	45.1	45.2	45.4	45.5	45.7	45.8	46.0	46.2	46.3
44	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2
45	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2
46	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2
47	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2
48	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1
49	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1
50	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1

B. In presence of 25 grams of sucrose in 100 ml.

Titer	100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L	0 D 100 L
15	42.9	43.1	43.2	43.4	43.6	43.7	43.9	44.1	44.3	44.5	44.7
16	42.9	43.0	43.2	43.3	43.5	43.6	43.8	44.0	44.2	44.4	44.6
17	42.8	42.9	43.1	43.2	43.4	43.5	43.7	43.9	44.0	44.2	44.4
18	42.7	42.8	43.0	43.1	43.3	43.4	43.6	43.8	43.9	44.1	44.3
19	42.7	42.8	42.9	43.1	43.2	43.3	43.5	43.6	43.8	43.9	44.1
20	42.6	42.7	42.9	43.0	43.1	43.2	43.4	43.5	43.7	43.8	44.0
21	42.5	42.6	42.8	42.9	43.0	43.1	43.3	43.5	43.6	43.7	43.9
22	42.5	42.6	42.8	42.9	43.0	43.1	43.2	43.4	43.5	43.7	43.8
23	42.4	42.5	42.7	42.8	42.9	43.0	43.1	43.3	43.4	43.6	43.7
24	42.4	42.5	42.6	42.7	42.8	42.9	43.0	43.2	43.3	43.5	43.6
25	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.1	43.2	43.4	43.5
26	42.2	42.3	42.4	42.6	42.7	42.8	42.9	43.0	43.2	43.3	43.4
27	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.1	43.2	43.3
28	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	43.0	43.1	43.2
29	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.0	43.1
30	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.0
31	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9
32	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9
33	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8
34	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7
35	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6
36	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6
37	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5
38	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5
39	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4
40	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3
41	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2
42	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1
43	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1
44	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0
45	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9
46	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8
47	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7
48	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7
49	40.6	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6
50	40.5	40.6	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5

effect than in the absence of sucrose, it is found that the precision is not quite as high as when reducing sugars alone are present, but it is nevertheless satisfactory for routine analyses of raw sugars.

TABLE II. DETERMINATIONS OF TOTAL REDUCING SUGARS BY LANE AND EYNON'S METHOD

10 GRAMS OF SUCROSE IN 100 ML. OF SOLUTION								
Dextrose taken, mg.	120.0	108.2	70.5	125.0	43.5	43.6	72.7	64.1
Levulose taken, mg.	137.9	65.7	150.5	125.0	138.0	82.0	36.0	186.9
Total	257.9	173.9	221.0	250.0	181.5	125.6	108.7	251.0
Titer found, ml.	18.15	26.6	21.4	18.6	25.9	36.9	42.5	18.8
Total found, mg.	258.4	172.9	219.6	251.6	180.3	124.7	106.8	251.6
25 GRAMS OF SUCROSE IN 100 ML. OF SOLUTION								
Dextrose taken, mg.	237.9	156.0	85.5	156.5	123.0	41.5	56.5	50.0
Levulose taken, mg.	37.5	132.5	106.3	56.0	53.7	86.5	47.8	98.5
Total	275.4	288.5	191.8	212.5	176.7	128.0	104.3	148.5
Titer found, ml.	15.6	15.2	22.35	20.3	24.0	33.05	40.25	28.7
Total found, mg.	276.3	287.2	192.8	211.8	178.3	128.6	103.6	149.1

The use of Jackson and Mathews' modification of Nijns's method for the determination of levulose was next investigated from the standpoint of raw sugar analysis. An electrically heated water bath, with automatic thermostat control within 0.1° C., was employed for the purpose, and the directions of Jackson and Mathews were followed, except that 250-ml. flasks had to be used instead of the 150-ml. size which is no longer on the market. The reduced copper was determined gravimetrically, as in the previous investigation. A number of analyses were made with different quantities of levulose, and the bath temperature was so regulated that after 75 minutes' heating the results checked with those given in Jackson and Mathews' table. This was found to be the case when the water surrounding the immersed portion of the flasks indicated 55.2° C.

TABLE III. ANALYSES OF SUGAR MIXTURES BY A COMBINATION OF METHODS

	Taken			Found				
	Sucrose	Levulose[a]	Dextrose[a]	Copper	Copper corrected for sucrose	Lane & Eynon titer	Levulose	Dextrose
	G./20 ml.			Mg.	Mg.		%	%
1	5	0.50	0.00	85.9	76.9	34.0	0.49	0.01
2	5	0.375	0.125	67.7	58.7	33.8	0.38	0.13
3	5	0.25	0.25	47.5	38.5	33.6	0.26	0.25
4	5	0.125	0.375	27.8	18.8	33.5	0.12	0.38
5a	5	0.00	0.50	8.4	−0.6	33.5	−0.05	0.55
5b	5	0.00	0.50	8.4	3.8	33.5	0.00	0.50
6	4	1.00	0.00	142.8	134.3	46.0	1.01	−0.01
7	4	0.75	0.25	108.5	100.0	45.8	0.75	0.25
8	4	0.50	0.50	73.2	64.7	45.4	0.49	0.52
9	4	0.25	0.75	42.1	33.6	44.5	0.24	0.77
10a	4	0.00	1.00	11.3	2.8	44.2	−0.05	1.06
10b	4	0.00	1.00	11.3	6.7	44.2	0.00	1.01
11	5	1.50	0.00	266.9	257.9	31.5	1.50	−0.02
12	5	1.125	0.375	207.0	198.0	30.5	1.11	0.41
13	5	0.75	0.75	142.9	133.9	30.6	0.75	0.75
14	5	0.375	1.125	84.2	75.2	30.6	0.39	1.10
15a	5	0.00	1.50	21.8	12.8	30.0	−0.07	1.58
15b	5	0.00	1.50	21.8	17.2	30.0	0.02	1.49

[a] Per cent of sucrose.

Mixtures of levulose and dextrose in varying proportions, with 4 and 5 grams, respectively, of sucrose in 20 ml. total volume were analyzed next, and the corrections established by Jackson and Mathews for the effect of dextrose and sucrose were confirmed. One milligram of levulose has the same reducing power as 12.4 mg. of dextrose; 4 grams of sucrose reduce 8.5 mg. of copper, and 5 grams of sucrose 9.0 mg. of copper. When no levulose is present, however, the reducing effect of sucrose is much smaller. Jackson and Mathews found that 5 grams of sucrose alone give only 2.4 mg. of copper; the writers found 4.6 mg. copper reduced by 5 grams of sucrose plus 25 mg. of dextrose, or 4 grams of sucrose plus 40 mg. of dextrose. This is of little importance in the analysis of raw sugars, because these always contain a certain proportion of levulose.

To test the combination of the Lane and Eynon and the Jackson and Mathews methods, mixtures of sucrose with 0.5, 1.0, and 1.5 per cent of total reducing sugars were prepared and analyzed as outlined above. In the case of the mixtures containing 1.5 per cent of total reducing sugars the Lane and Eynon titration was carried out after diluting 100 ml. of the original solution to 250 ml., and figuring back to the original concentration. The results, calculated as described by Jackson and Mathews, are shown in Table III.

For an indirect method, the results are satisfactory. When dextrose alone is present in addition to sucrose (Nos. 5, 10, and 15), the correction of 8.5 and 9 mg. of copper for the sucrose effect (*a*) is too high. A correction of 4.6 mg. in Nos. 5*b* and 10*b* gave zero levulose, in 15*b* 0.02 per cent of levulose; for 5 grams of sucrose and 1.5 per cent of dextrose (No. 15), the proper correction is 7.3 mg. of copper.

PROCEDURE

A number of raw cane sugars were next analyzed by the following procedure:

A solution of the raw sugar, containing 25 grams of sucrose in each 100 ml. is prepared (the direct polarization may be taken to equal the sucrose in most cases without serious error). A total of 250 ml. of solution is usually sufficient. The solution is clarified with neutral lead acetate solution before being made up to the mark. It is filtered, deleaded with dry potassium oxalate, and refiltered. Two 20-ml. portions of the final solution are used to determine in duplicate the reducing effect on the copper carbonate solution, according to Jackson and Mathews. The copper in the precipitate is determined volumetrically by Mohr's ferric sulfate and permanganate method, since weighing usually gives too high results because of contamination; electrolytic reduction, or the chromic acid–ferrous sulfate method of Jackson and Mathews may also be used. The remainder of the filtrate is used for the Lane and Eynon titrations, and the factor is found from Table IB. If the titer is less than 15 ml., 100 ml. of the clarified solution are diluted to 250 ml., the new solution now containing 10 grams of sucrose in 100 ml., and the factor is found from Table IA. If, on the other hand, the titer of the original clarified solution is over 50 ml., a new solution of the raw sugar is prepared and a known quantity of levulose or invert sugar is added, as suggested for such cases by Eynon and Lane (*2*). The added reducing sugar is later corrected for.

CALCULATIONS

The method of calculation is shown in the following example:

Sucrose, per cent in raw sugar	96.75
Grams of raw sugar containing 100 grams of sucrose	103.36

A sample of 64.60 grams of raw sugar (103.36 × $^5/_8$) was dissolved in a 250-ml. flask, and clarified as described above. The Lane and Eynon titer was found to be 18.13 ml. Since the ratio between levulose and dextrose is not known as yet, the first calculation is based on the factor for invert sugar in Table IB, which is 43.4. This gives 100 × 43.4/18.13 or 239.4 mg. of total reducing sugars, as invert, in 100 ml. of solution.

With the Jackson and Mathews method 76.9 mg. of reduced copper were found. Corrected for the reducing effect of the sucrose, this gives 76.9 − 9.0 or 67.9 mg. of copper. According to Jackson and Mathews' table, this corresponds to 22.0 mg. of apparent levulose in 20 ml. of solution, or 110.0 mg. in 100 ml. of solution.

	Mg.
Total reducing sugars as invert	239.4
Apparent levulose, first approximation	110.0
Apparent dextrose, first approximation, 239.4 − 110.0	129.4
Equivalent levulose, 129.4:12.4	10.4
Apparent levulose, second approximation, 110.0 − 10.4	99.6
Apparent dextrose, second approximation, 239.4 − 99.6	139.8
Equivalent levulose, 139.8:12.4	11.3
Apparent levulose, third approximation, 110.0 − 11.3	98.7
Apparent dextrose, third approximation, 239.4 − 98.7	140.7

Table IV. Determinations of Levulose and Dextrose in Raw Cane Sugars

No.	Origin	Dextrose	Levulose	Total Reducing Sugars
		%	%	%
1	Cuba	0.542	0.382	0.924
2	Philippines	0.671	0.557	1.228
3	Hawaii	0.176	0.261	0.437
4	Puerto Rico	0.559	0.531	1.090
5	Florida	0.426	0.402	0.828
6	Santo Domingo	0.342	0.446	0.788

The levulose equivalent of the dextrose, 140.7:12.4, is again 11.3 mg., so that the figures for levulose and dextrose, third approximation, are not changed further.

The ratio between levulose and dextrose is thus found to be 98.7:140.7, or as 41:59. For this ratio Table IB gives a Lane and Eynon factor of 43.3 instead of 43.4, and the total reducing sugars are therefore not 239.4, but 238.8 mg. In this particular case a second calculation, on the basis of 238.8 mg. of total reducing sugars, is hardly necessary, because the difference is within the limits of error. If it is made, the second calculation gives 98.7 mg. of levulose and 140.1 mg. of dextrose in 100 ml. of solution or in 25.84 grams of raw sugar. The final result is therefore 0.382 per cent of levulose, 0.542 per cent of dextrose, 0.924 per cent of total reducing sugars.

The results of the analyses of this and other raw sugars are compiled in Table IV.

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Extraction of Gossypol from Cottonseed Meal

Effect of Moisture and Repeated Extraction with Ether by Different Procedures

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In a previous paper (*2*) data were presented showing that moisture both in the cottonseed meal and in the ether exerted a marked influence on the amount of gossypol which could be extracted. These data suggested that there is no definite limit between the ether-soluble and bound gossypol. More data are presented here to substantiate those results and to show further what occurs when cottonseed meal is repeatedly moistened and extracted with ether, and with ether saturated with water.

Initial charges of 75 grams of cottonseed meal were moistened or conditioned (*2*) by passing a vapor of condensing steam over thin layers of meal for 5 hours, or, more conveniently, the proper amount of water was mixed in with a mortar and pestle. The conditioned meal was extracted for 72 hours and the gossypol estimated by a recently published modified method (*1*).

Ether-Soluble Gossypol from Moistened Cottonseed Meal

The U. S. P. grades of ether (not for anesthesia) obtained from the General Chemical Company and J. T. Baker Chemical Company (designated in the text as G and B ethers, respectively) have consistently yielded discordant amounts of gossypol. Consequently, experiments were undertaken to determine the quantity of gossypol which could be extracted from the same cottonseed meal by the following procedure:

Group *a*, determinations 1 to 3 with G ether alone
Group *b*, determinations 4 to 6, with B ether alone
Group *c*, determinations 7 and 8, with B ether, 10 cc. of alcohol (95 per cent), and 5 cc. of water
Group *d*, determinations 9 and 10, with B ether and 5 cc. of water

Preliminary work showed that meal conditioned by increasing its moisture content yielded more ether-soluble gossypol upon successive moistening of the charge of meal and subsequent extraction. It was therefore decided to determine how much ether-soluble gossypol could be extracted from meal 1578, which had previously shown a total (bound and ether-soluble) gossypol content of 1.102 ± 0.006 per cent (*3*). The repeated conditioning and extraction of the charge was continued as long as appreciable amounts of gossypol could be obtained.

Table I. Gossypol Recovered from Moistened Cottonseed Meal by Successive Extractions with Ether by Different Procedures

(Average mg. of gossypol per 100 grams of meal)

Extraction Periods	Group *a* Moisture	Group *a* Gossypol	Group *b* Moisture	Group *b* Gossypol	Group *c* Moisture	Group *c* Gossypol	Group *d* Moisture	Group *d* Gossypol
	%	*Mg.*	%	*Mg.*	%	*Mg.*	%	*Mg.*
Average gossypol and moisture per determination								
1 to 6	20.2	16.0	19.4	24.7	19.5	38.0	20.3	37.7
7 to 14	24.0	7.1	25.8	5.7	27.4	3.5	30.1	4.8
15 to 17	26.2	1.0	24.5	2.1	24.4	1.8	24.6	0.9
Average total gossypol per determination								
1 to 6		96.1		148.2		228.2		226.0
7 to 14		56.5		45.2		28.3		38.3
15 to 17		3.0		6.3		5.3		2.7
Per cent		0.1556		0.1997		0.2618		0.2670

In the first six successive periods of extraction an average of 16.0 mg. of gossypol per determination was obtained by the G ether in group *a*, compared to 24.7 mg. by the B ether in group *b* (Figure 1 and Table I). The moisture content of the charges in these groups does not vary greatly and is adequate for the extraction.

Groups *c* and *d* yielded an average of 38.0 and 37.7 mg. of gossypol per determination, respectively, considerably more than groups *a* and *b*. This large difference is apparently due to the addition of water to the ether in the receiving flask, since the moisture content of the charges in the various groups is approximately the same. The discrepancy in the yield of gossypol for groups *a* and *b* compared

to *c* and *d* is distinctly shown by the total amount of gossypol obtained per determination during extraction periods 1 to 6 (Table I).

Neither brand of ether without the addition of water or alcohol yielded as much gossypol in groups *a* and *b* in periods 1 to 6 as in groups *c* and *d* where water and alcohol were used with the solvent. Therefore, beginning with the seventh period of extraction, with groups *a* and *b* 10 cc. of alcohol (95 per cent) and 5 cc. of distilled water were added to the ether in the receiving flask of each determination. This procedure is similar to that employed from the first extraction period on in group *c*.

The average amount of gossypol obtained in extraction periods 7 to 14 was small even with this change in procedure for groups *a* and *b*, and in comparison with periods 1 to 6 was considerably less for all groups. The average moisture in the charge was adequate and quite uniform except in group *d*, where it increased, especially in extraction periods 11 to 13, but an appreciably higher yield of gossypol did not accompany this increase in moisture. The yield of gossypol in group *a* with the changed procedure in extraction is somewhat increased over that of the other groups for the tenth, twelfth, and thirteenth periods, probably because of the smaller amount of gossypol obtained in the first six periods of extraction.

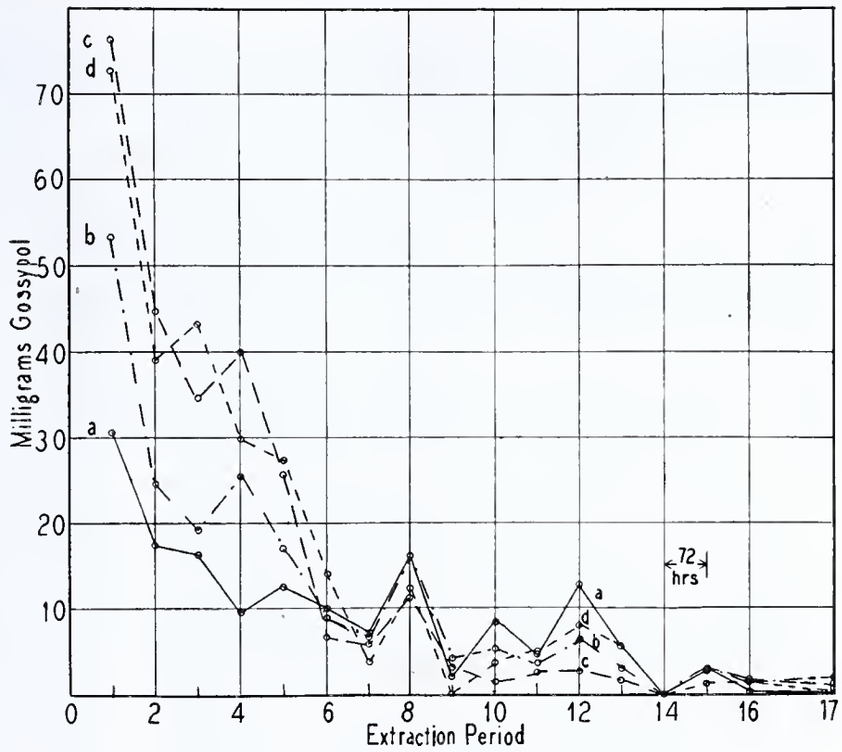

Figure 1. Average Gossypol Yielded by Groups *a* to *d* by Four Procedures of Extraction

The average amount of gossypol obtained per determination in extraction periods 7 to 14 for groups *a* to *d* does not vary much, but in groups *a* and *b* they are somewhat higher. The total amount of gossypol was less for groups *c* and *d*, although the moisture in the charge was somewhat higher for these groups than for groups *a* and *b*. With adequate moisture in the charge there is no correlation of yield of gossypol to moisture content.

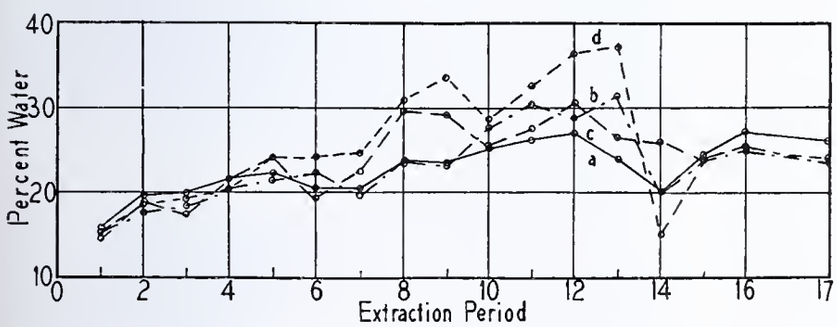

Figure 2. Average Moisture in Charge of Cottonseed Meal Extracted

Later, further extractions of the cottonseed meal residues were made, consisting of the fifteenth to seventeenth periods, with the result that for all four groups small weighable amounts of gossypol were obtained. The average gossypol obtained and the average moisture content of the charges are fairly uniform throughout for the groups (Figures 1 and 2).

The total gossypol recovered from the meal by the four procedures is 0.1556, 0.1997, 0.2618, and 0.2670 per cent, respectively. The amounts are appreciably higher in groups *c* and *d*, where water was always present in the flask containing the ether. The alcohol added to the solvent in group *c* did not show any beneficial effect in the presence of sufficient moisture in the charge. The presence of water in the receiving flask with the solvent causes the yield of gossypol to be larger but probably does not fully account for the difference in the behavior of the two brands of ether.

Of the total gossypol (1.102) in this meal, 24.2 per cent was gradually extracted by the ether in group *d* where water was always in contact with the solvent in the receiving flask.

Summary

Experiments show that by repeatedly extracting the moistened meal or residue with wet ether, considerably more gossypol can be obtained than by extraction of the air-dry meal or by a single extraction of the moistened meal.

By this procedure 24.2 per cent of the total gossypol in a sample of cottonseed meal has been gradually extracted. The amount of gossypol obtained by prolonged extraction shows that there is no definite limit between ether-soluble and bound gossypol. The gossypol formerly considered to be bound can be partially extracted as ether-soluble when there is sufficient moisture both in the meal and in the ether.

The amount of gossypol that can be extracted from an air-dry cottonseed meal (as has been done in the past) varies, depending chiefly upon the moisture content. Because the moisture content also changes at times, such results give no indication of the definite amount of gossypol present.

Probably the most reliable and practical indication of the amount of ether-soluble gossypol in cottonseed meal is obtained when the meal containing about 20 per cent of water is extracted for 72 hours with ether to which water has been added in the receiving flask. However, further extraction under these conditions will probably yield more gossypol.

Literature Cited

(1) Halverson, J. O., and Smith, F. H., Ind. Eng. Chem., Anal. Ed., **5**, 29–33 (1933).
(2) *Ibid.*, **5**, 320–5 (1933).
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Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen in Organic Substances

I. Analysis of Pure Compounds Containing Carbon, Hydrogen, and Oxygen, with and without Halogens

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A direct simultaneous micromethod has been developed for the determination of carbon, hydrogen, and oxygen in compounds containing these elements alone or with chlorine and bromine also present.

Ten substances have been analyzed, the mean precision of the oxygen determination being about 0.3 to 0.4 per cent. The precision of the oxygen determination is limited by the degree of precision obtainable in the carbon-hydrogen determination, any errors in the determination of the latter being multiplied by rather large factors. The oxygen consumed during the combustion is determined gasometrically with considerable precision.

The results of previous investigators using similar macro- or semi-micromethods have been critically analyzed and the discovery made that the apparently satisfactory results obtained by them were largely due to compensation of errors of considerable magnitude.

The investigation is being continued on more complex compounds and will finally be extended to the analysis of coal and its products.

THE lack of a satisfactory method for the direct determination of oxygen in organic substances and the potential value of such a method as a control on all of the other determinations made on a substance are generally recognized. Oxygen continues, however, to be almost universally calculated "by difference," despite the fact that this calculation involves, especially in complex substances, the summation of errors made in the determination of the individual components.

The published methods for the direct determination of oxygen may be grouped into the following five classes:

1. Complete oxidation of the substance by means of an inorganic oxidizing agent, followed by a determination of the amount of oxidant consumed (Table I).

Table I. Determination of Oxygen Using Inorganic Oxidizing Agents

Author	Inorganic Oxidizing Agent	Elements Present in Compounds Studied
Gay-Lussac and Thenard (*13*)	$KClO_3$	C, H, O, N
von Baumhauer (*1*)	CuO	C, H, O
Stromeyer[a] (*27*)	$CuO-Na_2CO_3$	C, H, O, N, S, Cl
Maumene[b] (*16*)	$PbO-Ca_3(PO_4)_2$	.....
Ladenburg (*15*)	$AgIO_3-H_2SO_4$	C, H, O
von Baumhauer (*2*)	$CuO-AgIO_3$	C, H, O, N
Mitscherlich[c] (*19*)	HgO	C, H, O, N, S, P, and halogens
Phelps[d] (*21*)	Chromic acid-H_2SO_4	C, H, O, N
Boswell (*5*)	CuO-asbestos	C, H, O
Strebinger[e] (*26*)	$KIO_3-H_2SO_4$	C, H, O, S, N, and halogens
Staněk and Nemes[f] (*24*)	$KIO_3-H_2SO_4$	C, H, O, S, N
Staněk and Nemes[g] (*25*)	$KIO_3-H_2SO_4$	C, H, O, S, N, and halogens

[a] Determined only oxygen consumed. Not applicable to nitro compounds or nitrates. Results always low.
[b] No data given.
[c] Technic very complex and tedious.
[d] Nitrogen compound studied gave the poorest result.
[e] Not applicable to nitrogen compounds which yield poor results on kjeldahlization—i. e., nitro-, azo-, and heterocyclic compounds, hydrazones, osazones, etc.
[f] A micromethod. Has same limitations as cited in subscript [e] plus halogens. Oxygen calculated by difference. Oxygen consumed determined directly. Hydrogen calculated by means of involved equations.
[g] Same as subscript [f] except difficulty due to halogens removed.

2. Destructive catalytic hydrogenation of the substance, followed by a determination of all resulting oxygen-containing substances (Table II).

Table II. Determination of Oxygen by Hydrogenation

Author	Elements Present in Compounds Studied
Wanklyn and Frank[a] (*28*)	.....
Boswell[b] (*6*)	C, H, O
ter Meulen[c] (*18*)	C, H, O, N, S, and halogens
Schuster[d] (*23*)	C, H, O, and coal
Dolch and Will[e] (*8*)	C, H, O
ter Meulen[f] (*17*)	C, H, O, and coal
van Beek and de Ward[g] (*3*)	C, H, O, N, S, and fuels
Will[h] (*29*)	.....
Russell and Fulton[i] (*22*)	C, H, O

[a] No data given.
[b] Five absorption tubes used requiring ten weighings. Slow. Not applicable to compounds containing less than 30 to 40 per cent of oxygen nor to compounds which yield easily condensable reduction products.
[c] A semi-micromethod. The most complete study on the determination of oxygen yet made. Somewhat complex when several elements are present besides carbon, hydrogen, and oxygen.
[d] Confirmation of ter Meulen method applied to pure compounds, but a criticism of method when used for analysis of coal.
[e] Criticism of ter Meulen method.
[f] Reply to Schuster and to Dolch and Will.
[g] Testimonial for ter Meulen's method.
[h] Reply to ter Meulen and to Schuster.
[i] Certain improvements made in ter Meulen's method.

3. Destructive deoxidation by a substance capable of uniting with the oxygen, followed by a determination of its increase in weight due to oxidation coupled with the determination of any oxygen-containing products which escaped reduction (*7*).

4. Destructive chlorination of the substance followed by a determination of the oxygen-containing gaseous decomposition products (*20*).

5. Complete catalytic oxidation of the substance in a stream of gaseous oxygen, the carbon dioxide and water formed being simultaneously determined, together with a quantitative gasometric determination of the "oxygen consumed."

The gasometric determination of the oxygen consumed in the complete combustion of an organic substance, first carried out by Lavoisier about 160 years ago, has recently been developed by Glockler and Roberts (*14*) using semi-micro technic. The data given by these investigators, who confined their studies to the analysis of benzoic acid and one hydrocarbon, show that the mean error of their carbon determination was −0.12 per cent and of their hydrogen determination +0.41 per cent. The mean error reported for oxygen was −0.69 per cent, despite the fact that the summation of errors made in the carbon-hydrogen determination should make their oxygen values high. An analysis of their

results revealed that their gasometric determination of oxygen consumed was inaccurate, generally being too high, this error overcompensating the effect of the errors in the carbon-hydrogen determination. No attempt was made to correct accurately the gas volume due to changes in temperature and pressure, and the apparent concordance of their results was largely due to fortuitous compensation of errors of considerable magnitude. The same criticism applies to the results reported by Dolch and Will (*9*) and Dumke (*10*).

After considering the results obtained by the above five methods, it was decided to attempt the further development of the fifth method. This method has the advantage that it simultaneously determines carbon, hydrogen, and oxygen. However, considerably greater precision is necessary in both the carbon-hydrogen determination and in the gasometric determination of oxygen consumed than has yet been reported. It should be emphasized that in this method the determination of carbon and hydrogen must be very precise, since errors of 1 per cent in hydrogen and carbon cause errors of 8 and 2.67 per cent, respectively, in oxygen.

For the purpose of this laboratory it was necessary to employ a micromethod using samples weighing about 10 mg. The present paper reports the results obtained with the micromethod applied to compounds containing carbon, hydrogen, and oxygen, with and without halogens. A later report will present the results obtained in the analysis of more complex substances containing nitrogen and sulfur, and on coal.

Microdetermination of Carbon and Hydrogen

Pregl's combustion apparatus was modified for this determination as follows:

Absorption Tubes. The absorption tube fillings recommended by Pregl were not used in the present case because the tubes have to remain connected with each other and with the combustion tube for much longer periods than is customary in ordinary microcombustion practice. The use of absorbents for water—such as calcium chloride, dehydrite, anhydrone, etc., which depend upon hydrate formation—was avoided and instead phosphorus pentoxide deposited on pumice was used, as recommended by Boëtius (*4*). Ascarite was used for absorption of the carbon dioxide. Both of these fillings have the advantage that one can tell at a glance to just what extent they have been exhausted. The absorption tubes were stoppered with tight-fitting pins during weighing, as recommended by Boëtius, and were weighed filled with oxygen.

Combustion Tube. Pregl's so-called Universal filling was first used, but on attempting to carry out blank quantitative oxygen transfers through the heated combustion tube, it was found that as much as 2 cc. of oxygen disappeared during each experiment. By a process of elimination, the loss of oxygen was traced to the copper oxide–lead chromate portion of the tube filling. Since the other portions of the Pregl filling were found to introduce no errors in the gas transfer, they were retained and it was merely necessary to replace the copper oxide–lead chromate filling with some other substance which would not cause this error. The successful use of a catalytic method in both macro- and micromethods (*12*) of combustion analysis suggested its trial for the present purpose. It was found that a 40 per cent palladium-asbestos catalyst, when used with the other reagents recommended by Pregl, gave accurate results for carbon and hydrogen. To insure complete combustion, the vaporization of the sample must be conducted somewhat more carefully than usual, since in this case the oxidation must all be done by gaseous oxygen which passes through the tube during the combustion. Further details of this method including the results obtained and a discussion of the advantages will be presented in a separate communication from this laboratory.

Purifying Train. Commercial oxygen, 99.5 per cent pure, was taken from a high-pressure tank and stored in a Haack Universal gasometer. From here it passed successively through a Pregl pressure regulator (*A*, Figure 1); an electrically heated Böck-Beaucourt platinum-asbestos purifier, *B*, which oxidized impurities; a spiral cooler; a large U-tube, *C*, the first arm being filled with Ascarite and the second with phosphorus pentoxide on pumice; a Friederich flowmeter, *D*, adjusted to permit 3 to 4 cc. of oxygen to pass per minute; a small U-tube, *E*, filled like the large one; and thence into the combustion tube. It was necessary to replace the Pregl bubble counter by the Friederich flowmeter since the bubble counter formed a liquid seal which prohibited free diffusion of the oxygen in the closed system.

Apparatus for Determining Oxygen Consumed during a Combustion

This apparatus is a combination of some of the features contained in the work of Glockler and Roberts, Dolch and Will, and Dumke and is shown schematically in Figure 1. The principle of the method consists essentially in carrying out the combustion in a closed system of known volume and in determining the oxygen consumed and the oxygen in the combustion products. To determine the oxygen consumed it is necessary to have the system at known equilibrium conditions of temperature and pressure both at the beginning and the end of the combustion.

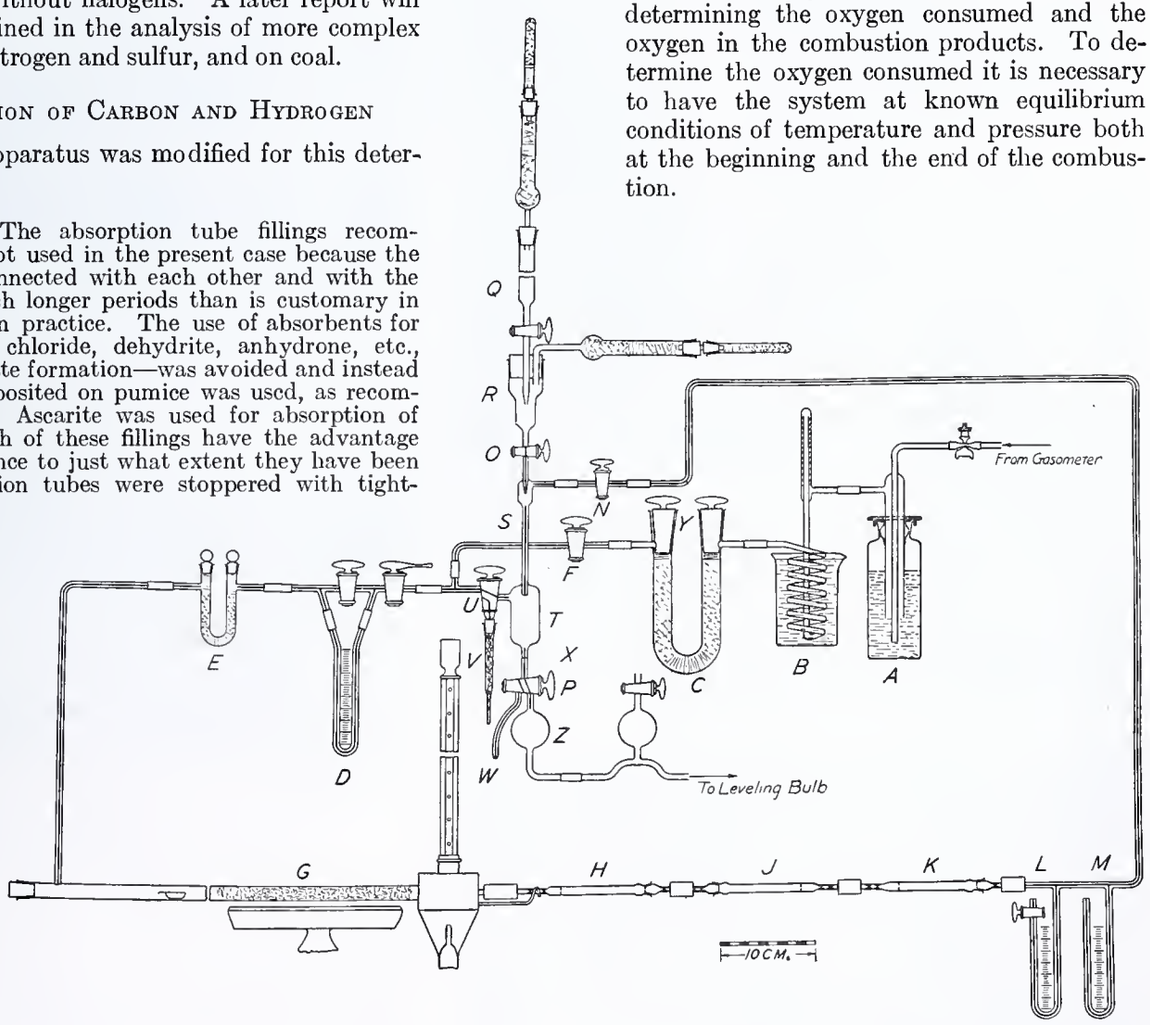

Figure 1. Schematic Representation of Apparatus

Circulation of the oxygen over the sample during the combustion was maintained by means of the Sprengel pump *OSTP*, the rate of pumping being controlled by the rate of admission of mercury through stopcock *O* from a constant-level tube, *R*, supplied by a 100-cc. buret, *Q*. The oxygen from the pump is delivered to bulb *T* and thence through the flowmeter, combustion and absorption tubes, manometers, and back to *N*. The combustion of the sample is thus carried out by means of this

known volume of oxygen present in the system. As the oxygen is consumed during the combustion, it is displaced by mercury which collects in *T*. The total amount of oxygen finally consumed is then determined, after temperature and pressure equilibration, by running mercury out of bulb *T*, through the side tube, *W*, attached to stopcock *P* until the level reaches the scratch, *X;* the mercury is then weighed. From the weight of mercury thus obtained, the volume of oxygen which it has displaced can be calculated. The water and carbon dioxide formed during the combustion are absorbed in tubes *H* and *J* and from their increase in weight the oxygen content of these products can be calculated. With these data available, the oxygen in the sample can be calculated and is equal to the oxygen in the combustion products minus the oxygen consumed.

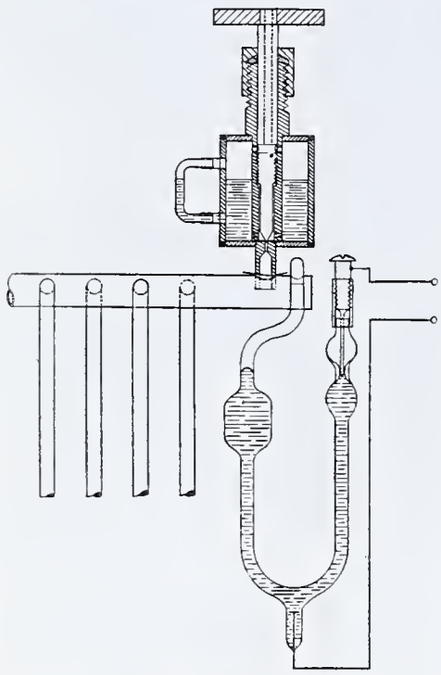

Figure 2. Thermoregulator Valve and Thermoregulator

Determination of Volume of Closed System. In order to calculate accurately the weight of oxygen consumed during a combustion, it was necessary either to carry out the analyses under constant initial and final conditions of temperature and pressure, or else to determine these conditions accurately at the beginning and end of each experiment and to know the volume of the apparatus. The latter alternative was the simplest, and so the volume of the closed system was determined by means of pressure-volume measurements. Previous investigators have completely neglected this fact and consequently the values they give for oxygen consumed are inaccurate.

Since microsamples were burned, it was found that to get accurate results the total volume of the system had to be kept as small as possible, so that the volume of oxygen consumed during a combustion was an appreciable fraction of the total oxygen originally present. If this precaution was not taken, one encountered the difficulty of getting precise values from small differences in relatively large numbers.

In order to get accurately determinable initial and final conditions of temperature and pressure in the apparatus, the whole apparatus was surrounded by a practically air-tight wooden box which had removable glass front and top panels, so that the apparatus was, in effect, completely isolated from the room. Two small fans were mounted inside the box, at either end and not directly opposed, the motors being mounted outside the box so that the heat generated by them was dissipated outside the box. Temperatures were read to ±0.01° C. by means of two calibrated thermometers inserted through the top of the box, one just adjacent to the Sprengel pump and the second just above the butyl phthalate manometer, *L*. Barometric pressure was read on a precision Paulin barometer to ±0.1 mm. using a magnifying glass. The pressure in the apparatus was determined by means of the butyl phthalate manometer which was read to ±0.01 mm. of mercury. This manometer was provided with a stopcock so that it could be closed off during pumping periods or when the apparatus was not in use, thus avoiding the possibility of the manometer contents being sucked or blown out of the tube. A mercury manometer, *M*, also was used in the experiments on the determination of the volume of the apparatus and in controlling the pressure in the apparatus during pumping, and was read to ±0.1 mm. To avoid sticking, the mercury was lubricated with a small amount of butyl phthalate; it was found that before taking a reading it was necessary to shake the manometer slightly so as to wet the tube walls with the phthalate and thus lubricate the mercury columns. Since both manometers were in line with the air currents generated by the fans, the open ends of each were extended outside the box to atmospheric pressure.

In order to control the termperature in the box so that initial and final conditions were approximately the same, a thermoregulator and a pair of heaters were placed in the box. The temperature inside the box was brought a few degrees above that of the room and accurately maintained there to within ±0.02° C. After the combustion, the final temperature was made approximately that present initially.

The heaters consisted of nichrome coils mounted on a circular Transite support in front of each fan, so that when the current was on the heated air was immediately put into circulation. The thermoregulator (Figure 2) was made of very thin copper tubing in the form of a grid (total width 45 cm., height 32 cm., with 10 pairs of staggered uprights connecting the two horizontal feeders), and was filled with toluene. The thermoregulator actuated the heater through a vacuum tube–operated relay, in a circuit shown in Figure 3. By means of this apparatus constant temperatures more or less independent of the room temperature were obtained in the box after about 30 minutes.

Determination of Volume of Apparatus. The filled absorption tubes were put into position, completing the closed system, and oxygen was passed through the apparatus to displace any air, stopcock *U* being turned so that oxygen escapes to the atmosphere after passing through the entire apparatus; the entrance of moisture was prevented by the protection tube *V*. The stopcock on manometer *L* was closed during this operation. The side arm, *W*, was filled with mercury, the level of the mercury in the apparatus carefully adjusted to the scratch, *X*, and stopcock *P* closed. The oxygen from the supply gasometer was turned off, stopcocks *Y* and *F* were closed, the stopcock on manometer *L* was opened, the front and top sections of the constant-temperature box were put into place, the fans started, and the heating current was turned on.

When the desired temperature was reached, the valve on the thermoregulator was closed and the resistance in the heating circuit adjusted so that the on and off periods of the relay were approximately the same. The zero-point readings of the manometers *L* and *M* were checked and then stopcock *U* was turned so that the system was closed. No readings were taken for the first 30 minutes, the on and off times of the relay being maintained approximately the same by adjusting the resistances. At the end of 30 minutes readings were taken of the two thermometers, the phthalate manometer, and the barometer, and repeated at 40 and at 50 minutes. At the time of the last readings the position of the mercury level of the mercury manometer was taken with respect to the zero mark of the right arm. To insure that the changes in temperature and pressure in the apparatus had responded to the changes in the atmosphere surrounding it, pressure-temperature calculations were made for the 30-, 40-, and 50-minute readings and the calculated pressure values compared with those observed. For sufficient precision the agreement must be within 0.1 mm. Typical data and calculations are given in Table III.

When constant P-T conditions were obtained, as indicated by the agreement between the calculated and observed pressure values, the final temperature and pressure were noted and represented the equilibrium starting conditions. The starting pressure and temperatures given in Table III are 741.52 mm. and 299.29° K.

Table III. Pressure-Temperature Data

Reading	Temperature: Thermometer *A*	Temperature: Thermometer *B*	Temperature: Room	Pressure: Barometer	Pressure: Manometer *L*	Pressure: Manometer *R*	Mercury Level (*M*)
Min.	*° C.*	*° C.*	*° C.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*
30	26.18	26.14	23.7	741.6	+0.06	−0.04	...
40	26.20	26.18	23.8	741.6	+0.05	−0.03	...
50	26.20	26.18	23.8	741.6	+0.05	−0.03	+1.6

Pressure-Temperature Calculations

Reading Interval	P_2	T_2	T_1	P_2 (calcd.)[a]	P_2 (obsvd.)	Diff.
Min.	*Mm.*	*° K.*	*° K.*	*Mm.*	*Mm.*	*Mm.*
30–40	741.50	299.29	299.26	741.58	741.52	0.06
40–50	741.52	299.29	299.29	741.52	741.52	0.00

[a] P_2 is calculated from the equation: $P_2 = \frac{P_1 T_2}{T_1}$.

The heaters and fans were then turned off, the thermoregulator valve was opened, and the stopcock on manometer *L* closed.

The glass panel in front of the Sprengel pump was opened, the mercury in the leveling bulb raised until slightly above the level in the apparatus, and then stopcock P opened to permit mercury to enter bulb T on slowly raising the leveling bulb. This created a pressure in the entire apparatus which could be followed by its effect on the mercury manometer, M. When sufficient mercury had been added to give the maximum readable pressure on this manometer, stopcock P was closed, the heater and fans were again turned on, and the thermoregulator valve was again closed when the initial temperature was approximately reached. Establishment of equilibrium conditions was determined in the same manner as described in the preceding paragraph.

Since the increase in pressure in the closed system was caused by a decrease in the gas volume equal to the volume of mercury added to bulb T, it was necessary only to determine this volume of mercury in order to calculate from the initial and final equilibrium pressures and temperatures the volume of the closed system. The added mercury was run out through the side arm, W, and weighed, its volume being calculated from its density at the final temperature prevailing in the apparatus. The volume of the apparatus can then be calculated to the zero line of both manometers by means of the equation:

$$V = \frac{\frac{P_2T_1}{P_1T_2}(b - a)}{1 - \frac{P_2T_1}{P_1T_2}}$$

where V = volume of free space in the apparatus
P_1 = initial pressure in mm. of mercury
P_2 = final pressure in mm. of mercury
T_1 = initial temperature in ° K.
T_2 = final temperature in ° K.
a = volume of mercury added to system (calculated from the weight of mercury added)
b = sum of volumes added or subtracted by depression or elevation of the manometer fillings from the zero mark (1 mm. on mercury manometer = 0.00208 cc.; 1 mm. on butyl phthalate manometer = 0.00199 cc.)

The mean value obtained from five such determinations of the volume of the apparatus was 87.7 ± 0.27 cc. Greater precision was not necessary, since use was made of this figure only for correcting the volume of oxygen consumed because of changes of temperature and pressure in the conditions at the start and finish of the experiment. Also, since the small U-tube and absorption tube fillings were gradually exhausted, the volume gradually increased and on refilling the absorption tubes or the combustion tube it was impossible to fill them so that no change in volume occurred.

Quantitative Gas Transfer Experiments. With the volume of the apparatus known, a large number of blank experiments were made to determine the quantitative nature of the gas transfer. In these experiments no sample was burned, but otherwise the technic was identical to that which was used when a sample was being analyzed. It was found that in every experiment a small, fairly constant amount of oxygen was lost, the amount increasing if the time of pumping was increased. The average value of this loss for twenty-five experiments was 0.166 cc. at normal temperature and pressure.

Experiment showed that this loss was probably due to diffusion of oxygen through the rubber connections present in the apparatus, although all the glass ends at such connections were abutted. Using the equation given by Edwards and Pickering (*11*), the area which would have to be exposed to give a loss such as observed is about 5 to 6 sq. cm., an entirely reasonable figure considering that there were 19 such rubber connections present in the closed system through which the oxygen might have diffused. Since the loss mentioned (0.166 cc.) was found to be quite constant, this correction was applied in all the actual combustions.

Direct Microdetermination of Carbon, Hydrogen, and Oxygen

Procedure. The electrical heater was placed over the Böck-Beaucourt purifier and the current turned on so that the heater was at a dull red heat. The absorption tubes were attached and oxygen was passed through the apparatus and out through stopcock U. The mercury level in the Sprengel pump was accurately brought to the scratch, X. While oxygen passed through the cold combustion tube and displaced any air in the apparatus, a microsample for the combustion was weighed out, the amount depending somewhat on the percentage of oxygen in the sample.

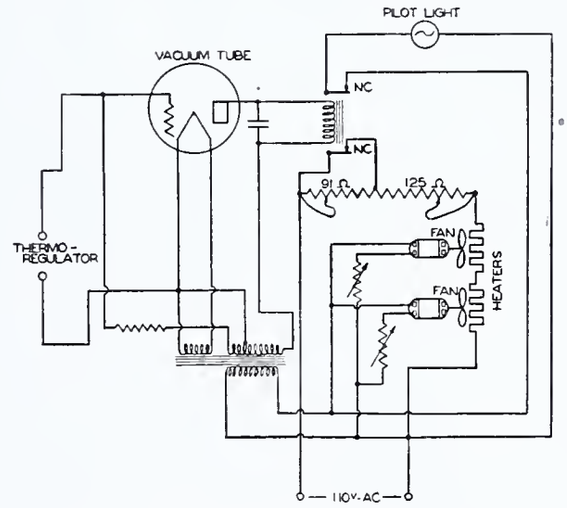

Figure 3. Electrical Circuit for Temperature Control

The absorption tubes were next removed, a phosphorus pentoxide protection tube was slipped over the tip of the combustion tube, a small glass rod slipped into the rubber tube covering the end of the phosphorus pentoxide tube, K, and stopcock U turned so that no air could enter, the apparatus being filled with oxygen under a slight pressure.

The absorption tubes were then wiped as usual, weighed after the appropriate interval, and replaced in the closed system. The sample was introduced into the combustion tube, while oxygen issued from the open end to prevent the entrance of moisture. The current to the electric heater was turned off and the heater removed from the box. Stopcock U was turned so that oxygen could again escape to the atmosphere. Stopcocks Y and F were then closed, the stopcock on manometer L was opened, the glass panels were put back so that the constant temperature box was tightly closed, the fans started, heat was turned on into the coils, and the oxygen coming from the supply gasometer turned off. When the desired temperature was reached in the box, the thermoregulator valve was closed. Since the apparatus was open to the atmosphere through stopcock U, atmospheric pressure should exist in the apparatus; a check was therefore made to insure that both manometers registered zero pressure. After the on and off periods of the relay had become regular and sufficient time had elapsed for most of the expansion to occur in the apparatus due to the temperature rise, the glass panel in front of the Sprengel pump was quickly opened and stopcock U turned to close off the system from the atmosphere. Pressure and temperature readings were taken until equilibrium was reached as determined by the criteria previously described. The current through the heating coils was then turned off, the thermoregulator valve opened, and the fans were stopped.

The middle top section and entire front of the constant temperature box were then removed, stopcock U turned so as to be completely closed, and the stopcock on manometer L closed. The leveling bulb was approximately leveled with the mercury at scratch X, and stopcock P turned to the position shown in Figure 1. Then the leveling bulb was lowered slightly until the mercury level in the apparatus was just at the bottom of the capillary below stopcock P. The long burner was then turned on low under the combustion tube and the expansion of the oxygen in the closed system forced mercury out into the expansion bulb, Z; any pressure generated was indicated on the mercury manometer and was avoided by occasionally lowering the leveling bulb and maintaining approximately atmospheric pressure in the apparatus. A Bunsen burner with a small

flame was then placed under the hollow mortar so as to bring its contents rapidly to the boiling point, gentle refluxing then being maintained by means of the microburner. The long burner was finally turned on full, keeping the pressure approximately equal to that of the atmosphere. Finally the movable burner was lighted, placed under the combustion tube at some distance behind the sample, and slowly turned up until it furnished the temperature desired; again, development of pressure was avoided.

After the tube had been heated for several minutes, stopcock *P* was closed and stopcock *U* opened to the system, the pressure by this time having been equalized so that on opening this stopcock no motion was observed in the levels of the flowmeter. The Sprengel pump was started and adjusted so that an oxygen flow of about 3.5 cc. per minute was registered on the flowmeter. The conditions of the oxygen circulation were practically identical to those recommended by Pregl—that is, there was a slight pressure of oxygen in the combustion tube proper and a slight vacuum (2 to 4 mm. of mercury) in the absorption tubes. Mercury shortly began to collect in the bottom of bulb *T* and increase in pressure was avoided by slightly opening stopcock *P* to expansion bulb *Z*, so that mercury left as rapidly as it entered.

With the oxygen circulating smoothly, the movable burner was pushed forward towards the sample, slowly and regularly, alternately moving the wire gauze around the combustion tube and the burner. In this way the sample was slowly melted, distilled, or sublimed, and finally vaporized completely into the hot tube where combustion occurred. As combustion took place, oxygen was used up which tended to decrease the pressure in the apparatus. A vacuum of greater than 2 to 4 mm. was avoided by intermittently closing stopcock *P* so that mercury replaced the oxygen consumed; the original conditions were thus maintained throughout the entire combustion, mercury gradually accumulating in bulb *T*. When the main part of the combustion was occurring and also when the products of combustion reached the absorption tubes, the oxygen was generally consumed at the same rate as mercury was added and during this time stopcock *P* was closed for a considerable length of time. If the vaporization of the sample was too rapid, a considerable vacuum was produced (as much as 30 to 40 mm.) and oxygen was consumed faster than mercury was added; in such cases it was usually found that low carbon-hydrogen values were obtained, the carbon particularly tending to be low because of incomplete oxidation. In general, the first combustion required about 75 to 85 minutes and the second (clean-up) combustion required about 15 minutes. After this the movable burner was turned out and oxygen was pumped for an additional 10 to 15 minutes. The complete time of pumping was thus 100 to 110 minutes. A total of about 60 to 65 cc. of mercury was added from the buret. During the entire combustion the mercury in the leveling bulb was kept at approximately the same level as the mercury in the expansion bulb.

The combustion was then stopped as follows: Stopcock *P* and then rapidly stopcock *O* were closed, leaving no drop hanging from the tip above *S*. Then, in order, the buret stopcock, stopcock *U*, and stopcock *N* were also closed, closing off the Sprengel pump completely from the rest of the apparatus. Stopcock *P* was then opened to the expansion bulb and some of the mercury ran out of bulb *T*. Oxygen was then transferred from the expansion bulb to bulb *T*, allowing more mercury to run out. This procedure was repeated until nearly all the mercury was removed from bulb *T* and capillary *S* completely cleared of mercury. The leveling bulb was then raised gradually until its level was a few millimeters above the level of the mercury in bulb *T* to avoid flow of oxygen out of the combustion tube; stopcock *U* was opened to the system, causing a slight flow of oxygen into the combustion tube. The long burner and microburner under the hollow mortar were turned off and the large wire tunnel over the combustion tube was removed. Any decrease in pressure in the system due to contraction of the oxygen on cooling was avoided by addition of mercury from the leveling bulb to bulb *T*. To hasten cooling, both fans were turned on and a stream of air was directed against the underside of the hollow mortar.

When the temperature of the apparatus had fallen to approximately that of the room, stopcock *N* was opened, stopcock *U* closed, and the stopcock on manometer *L* opened. Next, a vacuum of about 1 mm. of mercury was produced in the apparatus by lowering the leveling bulb and then stopcock *U* was again opened to the system. The top and front sections of the box were then put into place and the heaters turned on. By adjustment of the mercury level in bulb *T* by means of the leveling bulb, atmospheric pressure was maintained in the system. Equilibrium temperature and pressure were established following the same procedure as used for the initial conditions.

The heaters were then turned off, the thermoregulator valve was opened, the fans were stopped, the front of the box was removed, the manometer stopcock closed, stopcocks *Y* and *F* were opened after being sure that the pressure regulator was filled with oxygen, and then stopcock *U* was opened to the atmosphere and oxygen passed through the apparatus for a few minutes while preparations were made to weigh the absorption tubes. The absorption tubes were then removed, wiped, and weighed after the appropriate time interval. The combustion apparatus, under slight oxygen pressure, was closed off from the atmosphere by means of phosphorus pentoxide tubes and could stand several days without the necessity of any conditioning.

After the absorption tubes were weighed, oxygen was again started from the supply gasometer and mercury run out of the Sprengel pump through the side arm until the mercury level was again at the scratch, *X*, the mercury being collected and weighed. From its weight the volume was calculated from the density at the final temperature of the experiment. All the data necessary for the calculation of the percentage of carbon, hydrogen, and oxygen in the sample were thus available.

Results. Following the procedure outlined, determination of oxygen in seven pure compounds containing only carbon, hydrogen, and oxygen was first carried out. Then three compounds containing halogen were analyzed, two of them containing chlorine and the third containing both chlorine and bromine. To illustrate the method of calculation, the complete data are given for one of the compounds in Table IV.

Table IV. Illustrating Method of Calculation

	Mg.
Weight of sample (benzoic acid)	9.118
Weight of carbon dioxide found	23.079
Weight of water found	4.087
	%
Carbon dioxide, found	69.03
Carbon dioxide, theory	68.83
Difference	+0.20
Water, found	5.01
Water, theory	4.95
Difference	+0.06
	Cc.
Volume of oxygen at start (740.37 mm.; 299.20° K.)	87.713
Volume of oxygen at start, NTP	77.993
Volume of mercury added	13.838
Volume of oxygen at end (737.72 mm.; 300.09° K.)	73.864
Volume of oxygen at end, NTP	65.250
Volume of oxygen at end, NTP + correction (0.166 cc.)	65.416
Volume of oxygen consumed, NTP	12.577
	Mg.
Weight of oxygen consumed, found	17.973
Weight of oxygen consumed, theory	17.930
Difference	+0.043
Weight of oxygen in carbon dioxide, found	16.785
Weight of oxygen in carbon dioxide, theory	16.735
Difference	+0.050
Weight of oxygen in water, found	3.630
Weight of oxygen in water, theory	3.586
Difference	+0.044
Sum of oxygen in products of combustion, found	20.415
Sum of oxygen in products of combustion, theory	20.321
Difference	+0.094
Oxygen in sample, found (O_2 in products − O_2 consumed)	2.442
Oxygen in sample, theory (O_2 in products − O_2 consumed)	2.391
Difference	+0.051
	%
Oxygen in sample, found	26.78
Oxygen in sample, theory	26.22
Difference	+0.56

In Tables V and VI, which summarize the results obtained on 10 pure compounds, it is seen that the observed oxygen-consumed values are on the average too low by about 0.02 mg. The volumes are expressed to 0.001 cc. and calculated to 0.001 mg. (although the precision is not of this order), because the weighings were made to these limits and 0.001 cc. of oxygen weighs roughly 0.001 mg.

The tabulated data show that this method is capable of determining oxygen directly with a mean precision of about 0.3 to 0.4 per cent, this error apparently being independent of the percentage of oxygen in the sample. In order to get this precision, the determination of hydrogen must be accurate to within 0.05 per cent. With this error in hydrogen as a maximum, the error in the determination of carbon must be very small if one is to obtain a final precision of 0.4 per cent. The rather high multiplication of error is an inherent

Table V. Microdetermination of Carbon, Hydrogen, and Oxygen in Compounds Containing Only These Elements

Compound	Weight of Sample	Found C	Found H	Found O	Found O_2 consumed	Difference from Theory C	Difference from Theory H	Difference from Theory O	Difference from Theory O_2 consumed
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*
Benzoic acid	9.118	69.03	5.01	26.78	17.973	+0.20	+0.06	+0.56	+0.043
	11.384	68.80	4.99	26.06	22.426	−0.03	+0.04	−0.16	+0.040
	9.203	68.81	5.01	26.70	18.087	−0.02	+0.06	+0.48	−0.010
Benzalacetophenone	7.321	86.42	5.83	8.09	19.666	−0.08	+0.02	+0.40	−0.036
p-Phenylphenol	7.088	84.54	5.95	9.59	18.648	−0.13	+0.03	+0.18	−0.022
	7.754	84.42	5.98	10.14	20.351	−0.25	+0.06	+0.73	−0.074
p-Cyclohexylphenol	6.965	81.48	9.18	9.68	19.536	−0.28	+0.02	+0.59	−0.079
	7.810	81.76	9.19	9.59	21.979	0.00	+0.03	+0.50	−0.015
Methyl-β-naphthyl ether	7.139	83.56	6.38	10.63	18.766	+0.06	0.00	+0.51	−0.021
	7.331	83.33	6.37	10.22	19.246	−0.17	−0.01	+0.10	−0.046
Anthraquinone	9.611	80.70	3.94	15.75	22.172	−0.05	+0.06	+0.37	−0.001
	9.523	80.55	3.86	15.31	21.917	−0.20	−0.02	−0.07	−0.053
	8.130	80.73	3.94	15.58	18.779	−0.02	+0.06	+0.20	+0.023
Sucrose	9.324	42.14	6.46	51.46	10.465	+0.07	−0.02	+0.02	+0.001
	13.605	42.15	6.47	51.41	15.288	+0.07	−0.01	−0.03	+0.020
					Mean =	−0.06	+0.03	+0.29 ± 0.04	−0.015 ± 0.005

Table VI. Microdetermination of Carbon, Hydrogen, and Oxygen in Compounds Containing These Elements Plus Chlorine and Bromine

Compound	Weight of Sample	Found C	Found H	Found O	Found O_2 consumed	Difference from Theory C	Difference from Theory H	Difference from Theory O	Difference from Theory O_2 consumed
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*
o-Chlorobenzoic acid	9.390	53.67	3.28	21.47	13.867	−0.01	+0.06	+1.02	−0.053
	11.436	53.77	3.25	21.16	16.928	+0.09	+0.03	+0.71	−0.025
sym-Trichlorophenol	12.478	36.53	1.54	8.33	12.638	+0.05	+0.01	+0.22	−0.005
p-Chlorophenacyl bromide	12.400	41.18	2.64	7.24	15.315	+0.05	+0.05	+0.38	+0.016
					Mean =	+0.05	+0.04	+0.58 ± 0.04	−0.017 ± 0.008

fault of this method and is the limiting factor in obtaining higher precision. The presence of halogens in the sample adds no complications to the method, but reduces the precision of the oxygen determination.

It may be emphasized that this is the first time that a true micromethod has been attempted for the direct determination of oxygen. As is often the case, the micromethod has pointed out large sources of error in the macro- and semimicromethods previously described.

Acknowledgments

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Precise Measurement of Air Permeability of Paper. A sensitive instrument has been developed by the Bureau of Standards for measuring the rate at which air passes through paper and other porous materials in sheet form. A preliminary survey indicated that the most common sources of error in existing instruments for testing the air permeability of paper are leakage, especially at the edges of the specimen, fluctuations in driving pressure, lack of sensitivity, and restricted range. The new instrument contains a permeability cell of novel design, in which an annular cell surrounds the inner testing cell. The air flow is so regulated that there is no lateral pressure gradient at the boundary of the inner cell, and hence no leakage into or out of it. The pressure regulator is a form of automatic diaphragm valve designed to maintain a very steady pressure drop across the instrument. The amount of air, which in a given time reaches the inner cell by flowing through the specimen under the influence of this constant pressure difference, is measured with a capillary flowmeter containing four carefully calibrated capillary tubes. Results are reproducible on an identical area to within a few tenths of one per cent.

The range of the new instrument is about a thousand times that of most other instruments available for the purpose. It will accommodate materials of any thickness up to half an inch, and it is not necessary to cut them in order to make the test. Tests can be made rapidly, since the element of time is taken care of in the calibration and the duration of the test need not be measured. The test area is larger than is usually found in air permeability instruments, in order better to sample the material. The instrument is well adapted to the testing of leather and some other sheet materials.

Colorimetric Determination of Silica in Boiler Water

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INFORMATION (*3, 13*) on the formation and methods of prevention of silica boiler scale is becoming increasingly more important in considering the design of modern high-pressure steam plants. The analytical determination of silica is naturally of fundamental importance in the consideration of such problems and is capable of high accuracy (*6*), but the length of time required to complete the analysis is too long for certain types of investigations. In such instances one must resort to a more rapid method of analysis, such as colorimetry.

Solutions containing dissolved silica react with acid solutions of ammonium molybdate to form colored silicomolybdates; soluble phosphates and iron salts likewise form complex colored molybdates. The reactions (*1, 2, 4, 7–12, 14–16*) are complicated and, although various complex molybdates have been isolated and prepared in a pure state, their existence in solution is somewhat conjectural, owing to the important effect of the hydrogen-ion concentration on the various equilibria existing.

Apparatus. Two colorimeters were used, a 40-mm. Bausch and Lomb Duboscq type and a 50-mm. Hellige Duboscq. A Macbeth daylight lamp was used as the source of illumination. Hydrogen-ion measurements were made using the hydrogen-saturated calomel electrode and the quinhydrone-saturated calomel electrode combinations.

Standards. Picric acid and potassium chromate solutions have been used as permanent liquid standards. A spectrophotometric comparison (prepared by A. C. Hardy, Massachusetts Institute of Technology) of these liquids with a silicate solution is shown in Figure 1.

Reagents. Calcium chloride: 111 grams of c. p. anhydrous calcium chloride per liter of solution (1 *M*). Ammonium molybdate: 10 and 25 per cent solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Hydrochloric acid: concentrated acid and 1 to 1 acid (by volume). Blank tests should be made on these reagents for the presence of silica.

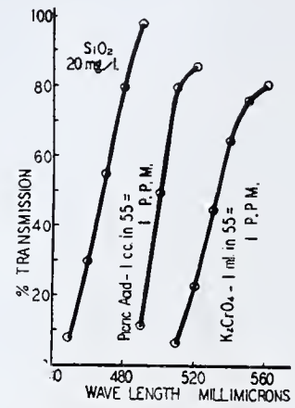

Figure 1. Spectrophotometric Comparison of Standards

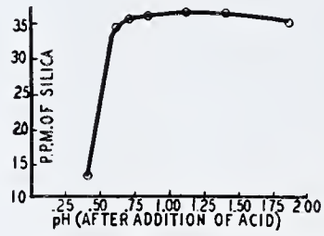

Figure 2. Effect of Varying pH on Color Intensity

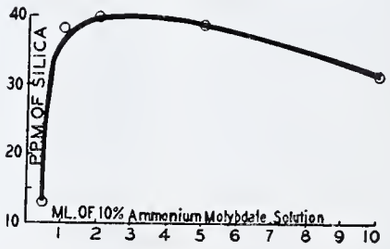

Figure 3. Effect of Ammonium Molybdate Concentration on Color Intensity

Figure 4. Effect of Time on Color Intensity

Experimental Results

Effect of Varying pH. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 2 ml. of 10 per cent ammonium molybdate solution and the various amounts of acid indicated in Table I to make up 50 ml. The colored solutions were compared with the appropriate silica standards standardized in a similar fashion against silica solutions. Figure 2 represents the data of Table I.

Table I. Effect of Varying pH on Color Intensity

Hydrochloric Acid	Apparent Silica Concentration	pH[a]
Ml.	*P. p. m.*	
0.25 (1 to 1)	35.0	1.85
0.5 (1 to 1)	35.9	1.39
1.0 (1 to 1)	36.7	1.12
1.5 (1 to 1)	36.0	0.85
1.0 Concentrated acid	35.5	0.71
1.0 Concentrated acid + 0.5 ml. (1 to 1)	34.5	0.62
2.0 Concentrated acid	13.8	0.41

[a] Determined with quinhydrone-saturated calomel electrode. The pH values although definitely reproducible are not precise measurements of hydrogen-ion concentration because of some reducing effect of quinhydrone on the silicomolybdate present in solution.

Effect of Ammonium Molybdate Concentration. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 1 ml. of a 1 to 1 solution of hydrochloric acid and the various amounts of molybdate solution indicated in Table II to make up 50 ml. Figure 3 represents the data of Table II.

Table II. Effect of Varying Ammonium Molybdate Concentration on Color Intensity

Molybdate Solution		Apparent Silica Concentration
Ml.	%	*P. p. m.*
0.5	10	13.3
1.0	10	38.2
2.0	10	39.7
2.0	25	38.6
4.0	25	32.0

Effect of Time. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 2 ml. of 10 per cent ammonium molybdate solution and 1 ml. of 1 to 1 hydrochloric acid to make up 50 ml. Figure 4 represents the data of Table III.

Table III. Effect of Time on Color Intensity

Time	Apparent Silica Concentration
Min.	*P. p. m.*
0	43.7
10	43.7
25	43.7
45	43.0
70	41.5
90	40.0

Effect of Initial pH. Either sodium hydroxide or hydrochloric acid was added to 125 ml. of boiler water to produce the desired initial pH. Two milliliters of calcium chloride solution were added and the solution filtered after 1 hour. Two milliliters of ammonium molybdate and 1 ml. of 1 to 1 hydrochloric acid were added to 50 ml. of sample. In some instances the volume and concentration of the acid added had to be varied to maintain a colorimetric pH value of about 1.1. Somewhere between a pH of 12.69 and 12.87 calcium hydroxide precipitates from the solution. Figure 5 represents the data of Table IV.

Effect of Buffer Solution. The quantities of buffer solution indicated in Table VI were added to 100-ml. samples of boiler water. The data of Table VI are represented in Figure 6.

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Table IV. Effect of Initial pH of Boiler Water on Error in Determining Silica

	Initial pH[a]	Silica Found	Error[b]	Final pH[c]
		P. p. m.	*P. p. m.*	
1	8.62	59.1	+18.1	0.98
2	9.24	48.9	+ 7.9	1.01
3	9.61	46.0	+ 5.0	0.99
4	9.97	41.1	+ 0.1	1.10
5	10.12	41.1	+ 0.1	1.09
6	10.32	41.2	+ 0.2	1.10
7	10.46	40.7	− 0.3	1.10
8	10.68	40.7	− 0.3	1.10
9	10.96	39.8	− 1.2	1.08
10	11.14	31.9	− 8.1	1.09
	11.14	31.3	− 8.7	0.76
11	11.53	10.1	−30.9	1.15
	11.53	Too faint to be read		0.30
12	12.10	3.7	−37.3	1.64
	12.10	4.4	−36.6	1.16
	12.10	4.2	−36.8	0.80
	12.10	Too faint to be read		0.52
13	12.37	<3.7	>37.3	1.24
	12.37	Too faint to be read		0.82
14	12.69	Too faint to be read		1.00
15	12.87	..	....	..
16	13.07	4.2	−36.8	1.88
	13.07	5.0	−36.0	0.66
17	13.58	16.8	−24.2	1.25
18	13.85	11.1	−29.9	0.28

[a] Determined with hydrogen-saturated calomel electrode.
[b] Average result of gravimetric analysis, 41.0 p. p. m.
[c] Determined with the quinhydrone-saturated calomel electrode, represents the pH value of the solution after addition of ammonium molybdate and hydrochloric acid.

Table V. Effect of Phosphate Precipitation on Initial pH of Boiler Water

Initial pH[a]	Equilibrium pH[a] (after Phosphate Precipitation)
9.61	7.36
9.97	7.38
10.12	7.69
10.32	7.84
10.46	7.92

[a] Determined with the hydrogen-saturated calomel electrode.

In order to determine the proper range of pH for phosphate precipitation more precisely, the fractional precipitation of calcium phosphate and silicate was investigated with the use of a series of buffer solutions (Table VII).

Table VI. Effect of Adding Borate–Sodium Hydroxide Buffer[a] Solution (*4*) on pH Values of Boiler Water

Buffer Solution Added	pH before Phosphate Precipitation[b]	pH after Phosphate Precipitation[b]
Ml.		
0	11.05	7.26
10	10.91	9.52
20	10.78	9.69
30	10.68	9.81
40	10.61	9.86
50	10.53	9.89
100	10.46	10.00

[a] Borate solution, 12.404 grams of H_3BO_3 and 100 ml. of *M* NaOH per liter. Sodium hydroxide solution, 0.1 *M*. The buffer solution consists of equal parts of borate and sodium hydroxide solution.
[b] Determined with hydrogen-saturated calomel electrode.

Fifty milliliters of buffer solution were added to 110 ml. of boiler water and the pH was determined. Two milliliters of calcium chloride solution were added and the solution was filtered after 1 or 2 hours. The pH was redetermined. Two milliliters of ammonium molybdate solution and 1 ml. of 1 to 1 hydrochloric acid were added to 50 ml. of solution and the silica and pH determined. The data of Table VIII are represented in Figure 7.

Table VIII. Colorimetric Determination of Silica in Boiler Water

(In presence of phosphate)

pH[a] of Buffer Solution	Initial pH[a]	pH after Pptn.[a]	Silica[b]	Error[c]	Final pH[d]
			P. p. m.	*P. p. m.*	
11.08	11.26	10.94	55.5	− 4.5	1.27
10.43	10.83	10.47	59.5	+ 0.5	1.25
10.26	10.61	10.29	58.8	− 0.2	1.25
9.92	10.12	9.94	59.6	+ 0.6	1.25
9.63	9.72	9.60	59.5	+ 0.5	1.25
9.41	9.48	9.40	59.4	+ 0.4	1.25
9.17	9.23	9.10	61.8	+ 2.8	1.25
9.02	9.13	9.00	62.5	+ 3.5	1.19
8.48	8.79	8.62	64.8	+ 5.8	1.14
8.04	8.46	8.28	68.0	+ 9.0	1.10
7.61	8.19	8.04	71.9	+12.9	1.04
7.27	8.02	7.83	75.0	+16.0	1.04

[a] Determined with hydrogen-saturated calomel electrode.
[b] Dilution factor, 1.54.
[c] Average result of gravimetric analysis, 59.0 p. p. m.
[d] Determined with quinhydrone-saturated calomel electrode.

Effect of Aluminum. Solutions of boiler water were prepared containing the proper amounts of aluminum and the initial pH was adjusted by adding hydrochloric acid. Two milliliters of calcium chloride solution were added. The sample was filtered after 1 hour and the pH determined. The silica was determined colorimetrically and the pH was determined again. The data of Table IX are represented in Figure 8.

Table IX. Effect of Soluble Aluminum on Colorimetric Determination of Silica in Boiler Water

Initial pH[a]	pH after Phosphate Precipitation[a]	Aluminum Added[b]	Final pH[c]	Silica[d]
		P. p. m.		*P. p. m.*
10.23	9.09	0	1.03	62.2
10.25	8.85	5	1.03	45.0
10.24	8.95	10	1.05	33.6
10.24	8.78	20	1.07	15.9
10.25	8.81	30	1.07	9.1
10.25	8.87	50	1.08	approx. 3

[a] Determined with hydrogen-saturated calomel electrode.
[b] Source of aluminum, aluminum chloride.
[c] Determined with the quinhydrone-saturated calomel electrode.
[d] Average result of gravimetric analysis, 64.2 p. p. m.

Table X. Effect of Iron on Colorimetric Determination of Silica in Boiler Water

Initial pH[a]	pH after Phosphate Precipitation[a]	Iron Added[b]	Silica[c]	Final pH[d]
		P. p. m.	*P. p. m.*	
10.24	9.72	0	61.3	1.04
10.24	9.75	2	61.1	1.05
10.22	9.75	5	60.5	1.04
10.26	9.73	10	52.5	1.04

[a] Determined with hydrogen-saturated calomel electrode.
[b] Source of iron, ferric chloride.
[c] Average result of gravimetric analysis, 63.0 p. p. m.
[d] Determined with quinhydrone-saturated calomel electrode.

Table VII. Buffer Solutions

Composition[a]	Expected pH	Actual pH[b]	Temperature	Reference (*4*)
			° *C.*	
75 ml. I + 75 ml. II	10.93	11.08	24	p. 208 (5 borate + 5 NaOH)
80 ml. I + 70 ml. II	....	10.43	25	p. 208
82.5 ml. I + 67.5 ml. II	10.36[c]	10.26	24	p. 208 (5.5 borate + 4.5 NaOH)
82.5 ml. I + 67.5 ml. II	10.36[c]	10.22	25	
90 ml. I + 60 ml. II	9.87	9.92	25	p. 208 (6 borate + 4 NaOH)
105 ml. I + 45 ml. II	9.60	9.63	25	p. 208 (7 borate + 3 NaOH)
120 ml. I + 30 ml. II	9.44	9.41	25	p. 208 (8 borate + 2 NaOH)
150 ml. I	9.19	9.17	24	p. 208 (10 borate)
135 ml. I + 15 ml. III	9.04	9.02	24	p. 209 (9 borate + 1 HCl)
97.5 ml. I + 52.5 ml. III	8.47	8.48	24	p. 209 (6.5 borate + 3.5 HCl)
37.5 ml. V + 112.5 ml. IV	7.94 (18°)	8.04	24	p. 213 (2.5 borate + 7.5 HCl)
18 ml. V + 132 ml. IV	7.46[c](18°)	7.61	23	p. 213 (1.2 borax + 8.8 H_3BO_3)
9 ml. V + 141 ml. IV	7.09 (18°)	7.27	23	p. 213 (0.6 borax + 9.4 H_3BO_3)

[a] Buffer solutions:
I, 12.404 grams of H_3BO_3 and 100 ml. of *M* NaOH per liter.
II, 0.1 *M* NaOH.
III, 0.1 *M* HCl.
IV, 12.404 grams of H_3BO_3 per liter.
V, 19.108 grams of $Na_2B_4O_7$.
[b] Buffer solutions were not prepared rigorously. Values determined with the hydrogen-saturated calomel electrode.
[c] Interpolated values.

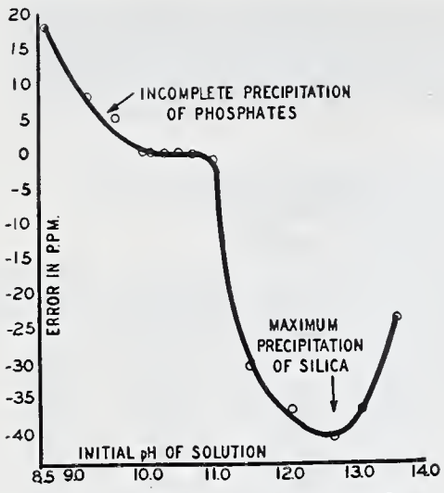

FIGURE 5. EFFECT OF INITIAL pH ON ERROR IN DETERMINING SILICA

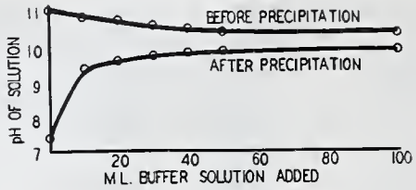

FIGURE 6. EFFECT OF BUFFER SOLUTION ON pH VALUES

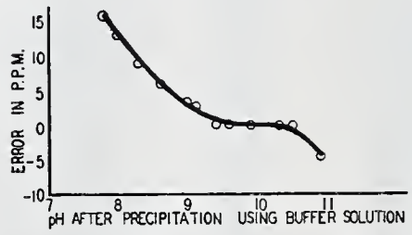

FIGURE 7. DETERMINATION OF SILICA IN PRESENCE OF PHOSPHATE

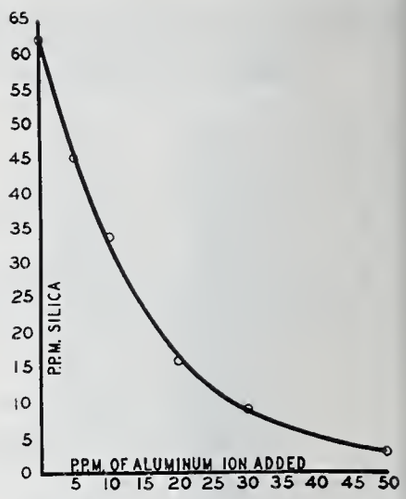

FIGURE 8. EFFECT OF SOLUBLE ALUMINUM ON COLORIMETRIC DETERMINATION OF SILICA

EFFECT OF IRON. Solutions of boiler water were prepared containing the proper amounts of iron and the initial pH was adjusted by adding sodium hydroxide. Where 2 p. p. m. of iron were added, a slight turbidity appeared, as well as precipitates in the subsequent samples. However, the solutions were not filtered. Two milliliters of calcium chloride solution were added. The sample was filtered after 1 hour and the pH determined. Silica was determined colorimetrically and the pH was redetermined. The data of Table X are represented in Figure 9.

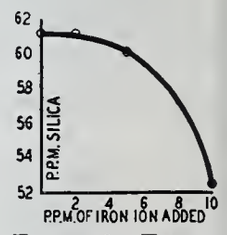

FIGURE 9. EFFECT OF IRON ON COLORIMETRIC DETERMINATION OF SILICA

SUMMARY OF RESULTS

The yellowish green color of the silicomolybdate complex (approximate silica concentration 50 p. p. m.) develops its maximum intensity (1) at a pH of approximately 1.1; (2) at a concentration of ammonium molybdate corresponding to approximately 2 ml. of a 10 per cent solution; (3) practically instantaneously if the molybdate and acid solutions are added in quick succession; and remains so for approximately one-half hour, after which it diminishes.

The precipitation of phosphates from boiler water by calcium chloride results in a drop in the pH of the solution.

The proper initial pH range of the boiler water for complete removal of phosphates without precipitation of silica is 9.5 to 10.5.

The use of a sodium hydroxide–borate buffer solution of pH 10 maintains the proper pH for the removal of phosphates.

The presence of aluminum in the boiler water as an aluminate reduces the determined silica concentration of the boiler water, particularly near pH values of 10, by actual reaction in the presence of calcium chloride.

Although very little iron can exist in solution in boiler water of pH approximately 11, the effect of adding iron on the colorimetric determination of silica has been determined as resulting in an apparent decrease probably due to adsorption of silica on ferric hydroxide.

PROCEDURE

As a result of the preceding work, the following reagents and procedure were developed:

SODIUM HYDROXIDE–BORATE BUFFER SOLUTION. Solution A, 12.40 grams of boric acid plus 100 ml. of *M* sodium hydroxide per liter. Solution B, 0.1 *M* sodium hydroxide. The buffer solution is made by taking 6 parts of solution A and 4 parts of solution B. The buffer is kept in a hard-rubber bottle.

CALCIUM CHLORIDE SOLUTION. 1 *M* calcium chloride.

AMMONIUM MOLYBDATE SOLUTION. Ten per cent solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

HYDROCHLORIC ACID. Three volumes of concentrated acid to 2 volumes of distilled water.

Calcium chloride, ammonium molybdate, and hydrochloric acid are kept in Pyrex glass bottles. Silica blanks should be taken on the reagents.

PROCEDURE. To 110 ml. of boiler water add 50 ml. of buffer solution, 2 ml. of calcium chloride solution, and stir vigorously. A flocculent precipitate of calcium phosphate forms which settles rapidly. Allow the solution to stand for approximately 2 hours (in any event, at least 1 hour) with occasional stirring, and then filter. To 50 ml. of the filtrate add 2 ml. of ammonium molybdate solution and 1 ml. of 3 to 2 hydrochloric acid solution. After allowing the solution to stand for 10 to 15 minutes, compare the silica color intensity with an appropriate potassium chromate or picric acid silica standard. Subtract the buffer blank from the calculated reading and multiply the result by the dilution factor (1.54).

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Received May 16, 1934. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934. The present paper includes a portion of a program of boiler feedwater research being carried out at the Louisiana Steam Generating Corporation under the general direction of E. B. Powell, Stone and Webster Engineering Corporation, Boston, Mass., with the coöperation of the Institute of Industrial Research, Louisiana State University, and with the collaboration of S. T. Powell, Baltimore, Md.

A Microscope Cold Stage with Temperature Control

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The microscopist may be called upon to examine a specimen below room temperature in order that he may observe temperatures, appearances, and optical properties of the specimen during freezing and thawing, transformation, or chemical reaction. The apparatus to be described consists of a cold stage and devices for controlling the temperature, and is designed for use at temperatures down to −25° C. and even lower. Accurate control of the temperature, to within 0.1° C., is considered important but means are also provided for quickly changing the temperature.

A simple cold stage has been described by Chamot and Mason (*1*), and was used in 1928 in her study of the freezing of emulsions by Miss Newcomer (*2*), who cooled the stage with alcohol, flowing by gravity through a cooled copper spiral. The present apparatus represents an improvement in the design of the circulatory system so as to include an air lift for pumping the liquid around the system and a shunt for more accurate control of the temperature of the stage.

Apparatus

Cold Stage. The cold stage, part *S* of Figure 1, may be made by any competent mechanic from a plate of aluminum about 70 × 100 × 10 mm.; the upper surface of this plate is channeled and a second plate, 3 mm. thick, is fastened tightly upon it by means of a lead foil gasket, *G*, and closely spaced screws. The channel thus constitutes a tube for circulation of a cooling agent through what is substantially a block of aluminum. An opening, 19 mm. in diameter, is provided for the specimen, and recessed at its edges to take windows of 25-mm. round coverglasses, the lower one sealed in place by vaseline. A hole for the reception of a low-temperature thermometer extends into the central chamber. The whole stage is insulated by 5-mm. sheet cork, held in place by pins and rubber cement. Several layers of aluminum foil, cemented by rubber cement, protect the insulation from sweating. The cold stage is clamped on any microscope having a fairly roomy stand, preferably after removal of the rotating stage.

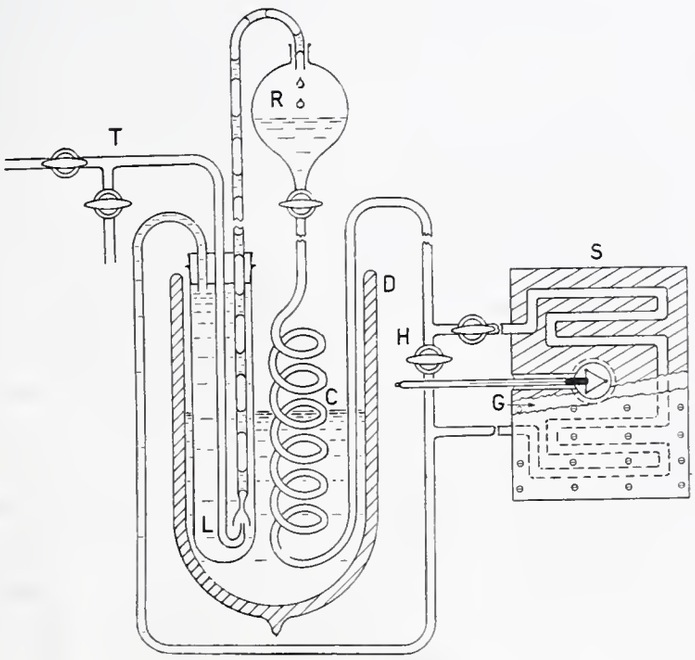

Figure 1. Diagram of Cold Stage and Cooling System

Circulatory System. The complete system for circulating cooled liquid through the stage is also shown in Figure 1. Dried air passes into the air lift, *L*, where the liquid of the cooling system is forced up into the reservoir, *R*. From there the liquid flows down into the cooling coil, *C*, and then either through the cold stage, *S*, or across the shunt, *H*, to return to the air lift, completing the circuit.

Air Lift. The air lift, *L*, is constructed as follows:

One end of a piece of 6-mm. glass tubing is drawn and bent into a curved nozzle with 2-mm. opening. Another piece of tubing is drawn out, 10 mm. from the end, into a neck about 25 mm. long and 3.5 mm. in diameter at its narrowest part. The bent nozzle is inserted into the second tube at the lower end of its constriction. The straight parts of the two members are separated by pieces of cork and are bound together by copper wire. The assembly is placed in a large test tube, 2.8 × 25 cm., which is filled with the liquid to be circulated and sealed with a rubber stopper with holes for the two tubes of the air lift and another hole for the return-line.

The air, admitted from a low-pressure air line, has its velocity further reduced by means of two stopcocks in a side-arm U-tube, containing calcium chloride for drying the air so as to avoid diluting the circulating liquid with condensed water from the air. A T-tube, *T*, with a stopcock in the branch, is inserted between the U-tube and the air lift.

The T-tube serves both as a safety outlet for any liquid which may be sucked back if the air pressure fails, and as a means for draining the apparatus of circulating liquid by applying air pressure at the top of the reservoir, *R*. The reservoir, a separatory funnel with stopcock, is about 50 cm. above the stage so as to provide static head for the liquid. In the operation of the air lift the air is admitted through the bent nozzle into the constricted tube at such a rate as to cause alternate slugs of air and liquid to rise in the delivery tube to the separatory funnel, from which the air escapes through a thistle tube (not shown) which also serves for the replacement of liquid lost by evaporation.

The advantages of the air lift as a pump in this apparatus are its simplicity of design and ease of construction; its high thermal efficiency due to the low conductivity of glass and air; its small size and convenient shape, permitting its placement in the cooling bath; its complete lack of moving parts; and the ease in the adjustment of the velocity of the circulating liquid.

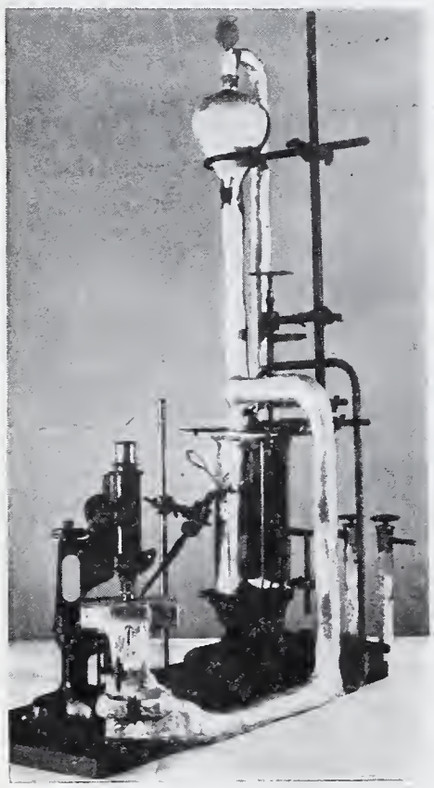

Figure 2. Cold Stage, as Used

The disadvantages of the air lift are loss of circulating liquid by evaporation before the system has been cooled appreciably; and the need for a chamber, such as a separatory funnel, in which to separate air from liquid, and where heat is transferred to the liquid despite insulation of the chamber.

From the reservoir, the liquid flows down into the cooling coil, *C*, of copper tubing, 6.5 mm. in outside diameter, wound into a spiral about 4 cm. in diameter and 18 cm. long. Both the coil and the air lift assembly are immersed in a cooling bath contained in a covered, silvered Dewar beaker, *D*, 12 × 27 cm. The authors recommend a cooling bath of acetone and solid carbon dioxide; about 4 pounds (1.9 kg.) will keep the stage at −15° for one afternoon.

The temperature of the stage is controlled chiefly by regulating the relative proportions of circulating liquid passing through the stage and through a shunt, *H*, which is across the inlet and outlet tubes. Control is by means of a pair of stopcocks, one in the outlet line and the other in the shunt line. Both are located near the stage for convenience to the observer.

In order to warm the specimen rapidly, a stream of dried air is directed against the upper window of the cold stage. The air is emitted from a glass nozzle connected to a glass stopcock which is attached to rubber tubing carrying a pinchcock near the glass stopcock. The stopcock is for fixing the velocity of the air at the nozzle, while the pinchcock is for releasing the air at the fixed velocity, whenever the observer wishes to arrest the cooling of the specimen or to raise its temperature quickly.

The units described are assembled as shown in Figure 2. The U-tube, Dewar beaker, air lift, cooling coil, and stirrer are all fastened to a large iron ring stand by means of iron clamps. The shunt and its stopcocks are mounted on a small wooden block, screwed to the baseboard. The cold stage is fastened to the microscope with an iron clamp. The microscope may be removed simply by unfastening the clamp and a single screw at the heel of the microscope base.

Lines for carrying air or circulating liquid are of 6-mm. glass tubing. The tubing carrying liquid is insulated with a layer of asbestos cement, approximately 1 cm. thick, and painted with powdered aluminum in lacquer to give a waterproof and reflecting surface. All glass tubing is fastened to the baseboard or to the larger parts of the apparatus, and thus, by having all the parts of the cold stage and its circulatory system fastened to the board, the apparatus is made portable as a unit.

Operation of Apparatus

By means of the apparatus described, the specimen in the cold stage may be cooled either slowly or rapidly and, likewise, warmed again either slowly or rapidly. If the specimen is to be cooled slowly it is placed in the stage at room temperature and the liquid is circulated, using the shunt so as to lower the temperature as gradually as desired. If the specimen is to be cooled rapidly the stage is first brought to the correct temperature and then the specimen is introduced into the stage. In either event, some of the liquid specimen should preferably make contact with the cold aluminum wall of the stage in order to give localized chilling; otherwise, the specimen being insulated all around by air, supercooling will be probable and final freezing may be too sudden. If the temperature of the specimen is to be raised gradually, the shunt and its stopcocks will serve the purpose. If a rapid rise in temperature is desired, or if cooling is to be arrested, the air current is released by pressing the pinchcock. The air may be preheated, if desired.

The specimen is mounted in a small watch glass or cell, or between two 18-mm. cover-glasses, and is supported above the lower window of the stage by means of a tiny wire tripod in close proximity to the bulb of the thermometer. If the tripod is 9 mm. high, the specimen is brought near enough to the upper glass window to permit the use of an 8-mm. objective (working distance, 1.5 mm.). After the specimen is in place the upper glass window is dropped in place, after being cleaned with Bon Ami and coated with a thin film of glycerol-water (1 to 1) to prevent fogging by condensed moisture from the atmosphere or air stream. With objectives of longer working distance an extra asbestos cover, 1.5 mm. thick, with a No. 3 cover-glass for window, may be placed over the well. With the stage and tripod of the given dimensions, dark-field illumination may be obtained by using an Abbe condenser with its top lens removed and equipped with a central stop of suitable diameter.

The authors recommend the Leitz objectives No. 2 (6X, 24 mm. focal length, 16 mm. working distance, 0.20 numerical aperture) and No. 3-b (14X, 13 mm. focal length, 3.2 mm. working distance, 0.40 numerical aperture). They are especially valuable for work with the cold stage because they combine long working distance with numerical aperture so high that even a 25X eyepiece will yield "useful" magnification.

Accuracy in Measurement of Temperatures

The cold stage and its circulatory system were designed primarily for qualitative examination of low-temperature phenomena; therefore it was considered most important to be able to maintain constant temperatures and to produce gradual changes in temperature. Quantitative measurement of freezing or transformation temperatures, however, is usually important. The freezing point of distilled water placed between cover-glasses in the well of the stage was

measured by an alcohol-filled thermometer graduated from +50° to −50° C. in degrees. With the bulb of the thermometer in the periphery of the field of a 6X objective and with the asbestos cover in place, readings for the temperature of ice, melting slowly or in equilibrium with water, were consistently 1.5° lower than those recorded with the same thermometer immersed in melting ice to the same extent as when in the cold stage; they were 2° lower than the freezing point indicated by "cooling curve" data. Undoubtedly a temperature gradient exists between top and bottom of the stage, and horizontal or vertical variations in the position of the thermometer bulb may also affect the temperatures it registers to the extent of one or two degrees.

Therefore a specific constant for the stage at a given temperature should be obtained by comparisons with pure compounds of known melting or transformation point, and with the thermometer in a definite location which should be maintained. The temperature at different places in the specimen is in reality reasonably free from any horizontal gradient, since freezing may start or progress equally well from any point.

Possible Improvements

Based on experience gained from three years' use of the apparatus described, the following modifications are suggested:

The cold stage might well be made thicker to provide a deeper well, so as to decrease the temperature gradient between top and bottom of the cell. The ledges for holding the windows should be made deeper; the bottom one so that the condenser may be brought nearer the object, the upper one so that objectives of shorter working distance may be used. The stage, as described, cannot be rotated as is desired between crossed Nicol prisms or in the measurement of angles. This limitation is removed if pieces of rubber tubing are inserted in the inlet and outlet lines near the stage, long enough to allow the stage to be rotated 45° to the left and right. The rubber tubing would also permit the horizontal movement of the stage so that more of the specimen might be explored than is possible by moving the cover-glass in the small free space between the cover-glass and the walls of the well.

By cementing the lower window in place, the well could be filled with liquid of low freezing point and immiscible with the specimen. Replacing the air in the well by a liquid would have the advantage of providing quicker and more uniform distribution of heat among stage, specimen, and thermometer. A circulation line of larger capacity, including larger tubing and stopcocks, would provide both quicker extraction of heat from, and lower possible temperatures of, the specimen. The return and feed lines could be shortened by placing the Dewar flask nearer the microscope and the shunt controls on the same side of the microscope as the Dewar flask.

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Sintered Glass Absorber for Determining Carbon by Wet Combustion

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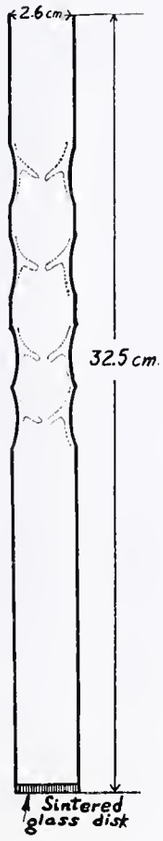
The method of Friedemann and Kendall (*2*) has been used for several years in the Color and Farm Waste Division for the determination of carbon in fermentation solutions, and is suited for this purpose except for the glass bead absorption column. This type of absorber is inherently inefficient, as Friedemann and Kendall have emphasized that a 50 per cent excess of alkali must be present to insure complete absorption of carbon dioxide. Moreover, it has been found difficult to wash the column of glass beads free of alkali, and ordinary glass beads after several weeks of use are so attacked by the alkali that they can no longer be used.

Various gas-washing bottles have been studied recently by several workers (*3, 4, 7, 8*), and the spiral and sintered glass (*5*) filter-plate types found to be the most efficient. Sintered glass disks of Pyrex glass can be made according to the method described first by Bruce and Bent (*1*) and more recently by Kirk, Craig, and Rosenfels (*6*). Thomas (*9*) found that the latter type of absorber was entirely satisfactory for absorbing carbon dioxide, provided a suitable surface tension depressant was added to the alkali. Butyl alcohol used for this purpose appreciably decreased the size of the bubbles and caused frothing, which was desirable. Using butyl alcohol in a concentration of 0.4 per cent, complete absorption of carbon dioxide was possible until practically all the alkali was neutralized.



This type of absorber seemed suitable for the authors' purpose because of its simplicity and its efficiency under the widely varying conditions which are possible. Because suitable commercial bubblers were not available, a number of disks for these absorbers were constructed somewhat after the method of Bruce and Bent (*1*), the principal variation being that a graphite mold (a type used with satisfaction for several years by the Fertilizer Investigation Laboratory of this bureau) was substituted for the nickel mold. The mold was approximately 5 cm. in diameter and 1 cm. thick, machined out centrally to a depth of 3 mm. and a diameter of 2.7 cm. No cover was needed. Ground Pyrex glass of 80-mesh size was tamped into the mold, after which it was placed in a muffle furnace heated to about 800° C. and allowed to remain for 2 minutes. The sintered disk can be removed immediately from this type of mold, and the mold is then ready for further use.

The type of absorption tower shown in the illustration was found best suited for the purpose. The indentations are necessary to prevent spray from being carried out of the tube. With a tube of this size and 50 cc. of solution, flows of air up to 100 cc. per minute can be used without danger of mechanical loss. The porosity of the disk, as well as the height and diameter of the tube, can be varied to suit individual needs.

The absorber was tested by the method of Friedemann and Kendall (*2*), in which it was substituted for the usual glass bead column. After complete combustion of the sample (30 minutes' digestion period) the absorber was raised to a convenient height above the bottom of the flask and the alkali washed out with hot water free from carbon dioxide. Usually three washings of 40 cc. each were sufficient. In order to hasten the washing, a hand aspirator connected with a soda-lime tube was used to force the water out of the absorber. The carbonate was then precipitated by adding barium chloride solution, and the stoppered flask was protected with a soda-lime tube while cooling. It has been found convenient to use a mechanical stirrer while titrating the excess alkali. To obtain consistent results, carbon dioxide-free air should be passed over the solution while titrating, particularly when using mechanical agitation, because otherwise air is drawn into the flask. Blanks should be run in exactly the same manner as the determination, to correct for carbon dioxide in the apparatus and reagents.

Table I. Determination of Carbon by Wet Combustion Using Sintered Glass Absorber

(Butyl alcohol added, 0.5 per cent)

Carbon Taken (as Sodium Oxalate)	Sodium Hydroxide Used in Absorber[a]	Per Cent of Original Sodium Hydroxide Unneutralized	Carbon Found
Gram			*Gram*
0.1435	0.5 *N*	4.2	0.1430
0.1436	0.5 *N*	4.2	0.1430
0.1435	0.5 *N*	4.2	0.1430
0.0722	0.5 *N*	51.8	0.0724
0.0717	0.5 *N*	52.2	0.0718
0.0719	0.5 *N*	52.0	0.0719
0.0278	0.1 *N*	7.4	0.0277
0.0277	0.1 *N*	7.6	0.0275
0.0279	0.1 *N*	7.0	0.0277

[a] 50 ml. used.

Typical results with the absorber described, given in Table I, show that the determination of carbon can be carried out successfully with complete absorption of carbon dioxide when less than 5 per cent of the alkali remains unneutralized. This was further evidenced by the fact that no precipitate appeared in a trap tube to which barium hydroxide solution (0.3 *N*) had been added and through which the air was passed after leaving the absorber.

Summary

The sintered glass absorber described has several advantages over the glass bead absorber previously used for this determination. It is unnecessary to maintain a large excess of alkali and consequently the method has a wider range of application. Washing the alkali from the absorber is easier. Difficulties due to the disintegration of the glass beads by the alkali are eliminated.

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A New Ultraviolet Microscope Illuminator

Preliminary Studies of Its Use with Rayons

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The analytical uses of fluorescence effects due to ultraviolet irradiations have been summarized by Danckwortt (*4*) and by Radley and Grant (*17*). Apparatus for both macro and micro observation has been built or suggested by Lehmann (*7*), Wasicky (*24*), Reichert (*18*), Naumann (*11*), Auer (*2*), Silverman (*21*), and Singer (*23*). One or more of the following factors limit the equipment cited above: the expense of quartz lenses, slides, and other accessories; unsuitability for both macro and micro investigations; lack of flexibility in making the microscope available for other work; lack of suitable ultraviolet intensity; and inability to use the higher powers of the microscope.

To eliminate these undesirable features as far as possible, it was decided to make use of an oblique cone of ultraviolet light impinging on the object, securing thereby an even and full illumination with the elimination of shadows, an increased depth of focus causing uneven structures to appear in relief, and the production of as true color values as can be obtained with artificial light. For visible light these results have been obtained with the Silverman illuminator (*20, 22*), Preston's top light illuminator (*15*), and the Leitz ultropaque (*8*). For fluorescence, the last named has secured these effects using glass equipment.

The apparatus described below was designed to secure still further advantages.

The apparatus consists of an enclosed annular quartz mercury arc (Figures 1 and 2). The experimental quartz model of the arc was built to the writers' specifications by the Hanovia Chemical and Manufacturing Co. This arc operates on line voltages from 110 to 220 direct current, with best results at about 155 volts, and a lamp bank resistance is used in series, such that the voltage drop across the arc is about 85 volts. From 1 to 2 amperes are required for starting, depending on the voltage.

The arc is mounted just above the stage, so that the objective can occupy the position shown in Figures 1 and 2. The mounting is light-proof except for the filters which transmit the ultraviolet rays to the object under examination. It is cooled by fins attached to the arc and by a circulating water system.

It is necessary to use a filter to remove as much as possible of the visible light emitted by the mercury arc (*4*), because its relative intensity obscures the fluorescence. The transmissivity of different filters may cause confusing phenomena. Thus Kögel (*6*) reported that certain filters transmit red rays which may be mistaken for red fluoresence. The published reports of fluorescence work often fail to specify what filters were used, and in most reports the use of only one filter is mentioned. To avoid the resulting confusion in reporting results, data obtained with a number of commercially available filters were recorded.

The best results with rayons were obtained by using Heat-

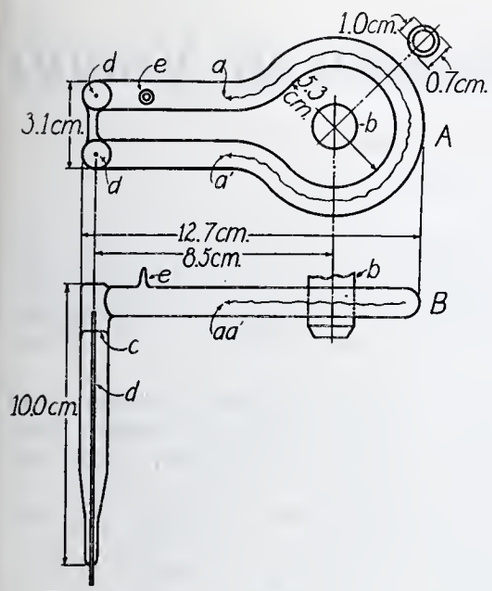

FIGURE 1. ANNULAR MERCURY ARC

A. Plan
B. Elevation
aa'. Luminous path of arc
b. Position of objective
c. Mercury
d. Tungsten electrodes
e. Evacuation tip (must be on cool part of arc)

Resisting Red Purple Ultra, No. 587 (*3*), and a combination of the Uvet Glas filters, Nos. 1 and 2 (*19*), possibly because of a suitable range in the ultraviolet, together with low intensity in the visible. In the case of Violet Ultra, No. 586 (*3*), the visible is nearly excluded, but no lines are shown with the mercury arc below 3300 Å. The results with this filter were poor, in accordance with the work of Lewis (*10*), who showed that the best region for the fluorescence of cellulose products lies in a region of shorter wave length. The silvered quartz filter completely excludes the visible, but is weak in the ultraviolet. Consequently, poor results were obtained with it.

FLUORESCENCE OF RAYONS

The chemical and microscopic methods (*1*) for the identification of rayons are still tentative. The chemical method is laborious. The use of fluorescence for identifying natural fibers (*5, 9, 13*) is fairly successful, but the results for rayon are conflicting (*12, 14, 16*).

The results obtained from the examination of thirty-seven undyed, unmordanted fibers, using the filters which gave the best results, are summarized in Table I. These fibers are authentic samples secured from the leading manufacturers of this country. The word "shadows" as used in the table refers to transmitted visible colors which simulate fluorescence, in accordance with the descriptions used by Nopitsch (*12*).

TABLE I. FLUORESCENCE CHARACTERISTICS OF RAYONS

Fiber	Filters: Heat-resisting red purple ultra, 587	Filters: Uvet glas-1 combined with uvet glas-2
Raw silk	Yellow to buff; brighter than nitrate rayons, paler than viscose	Yellow to buff, much brighter than nitrate and viscose rayons
Cuprammonium rayon	White with purple shadows; bright, whereas acetate rayons are dull	White; bright whereas acetate rayons are dull and tend to be tinted
Nitrate rayon	Pale yellow, without the brown tints present in silk or viscose	Dull, pale yellow without the brown tints in silk; distinction from viscose a matter of observer's experience
Acetate rayon	Dull, white, with or without tinted shadows; much less bright than cuprammonium rayon	Dull, white, usually with tinted shadows; much less bright than cuprammonium rayon, which is not tinted
Viscose rayon	Deep yellow to brown; deeper than the tints of nitrate rayon or raw silk; less bright than raw silk	Faint yellow to buff; easily distinguishable from raw silk; distinction from nitrate rayon a matter of observer's experience

Easily bleached dyed fibers gave substantially the same results as the undyed, and could be recognized even if a slight additional hue was present.

Mixed fabrics revealed the fluorescence of the constituent fibers microscopically, but showed macroscopically a single color which was a combination of the constituent hues. Although the same type of product made by different manufacturers shows slight differences in the tints obtained, these differences cannot be utilized for identifying the source of the fiber, because they may result from the fluorescence of impurities incidental to the manufacturing and finishing processes.

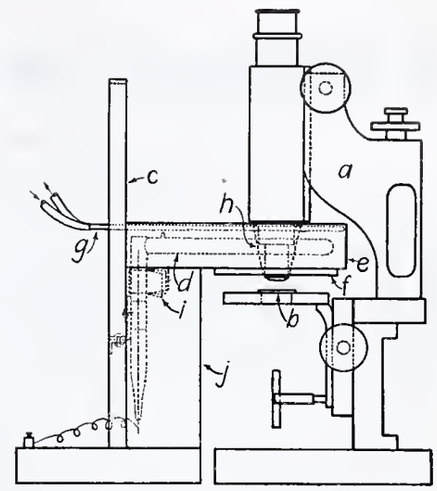

FIGURE 2. USE OF ANNULAR ARC WITH MICROSCOPE

a. Microscope
b. Slide
c. Arc support
d. Circular arc
e. Shield to enclose arc
f. Filter, 7.94 cm. (3.125 inch) square, with hole in center 1.7 cm. (0.67 inch) diameter. The filters slip into a slot for easy interchanging
g. Water cooling system
h. Metallic cone to shield objective from heat of arc
i. Cooling fins
j. Auxiliary shield

The method will require study of authentic samples by anyone contemplating using it because of the difficulty of exact description of the colors observed. Further work is desirable, not only for the study of specimens which are difficult to bleach, but also with other ways of treating fibers before testing.

ACKNOWLEDGMENT

The authors are grateful for the assistance rendered by W. N. St. Peter of the University of Pittsburgh and by the various manufacturers of silks and rayons.

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A Stillhead for Rapid Concentration in Vacuo

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Connecticut Agricultural Experiment Station, New Haven, Conn.

BIOCHEMICAL laboratories are frequently faced with the problem of concentrating large volumes of aqueous or alcoholic solutions. This is a time-consuming operation, especially when care must be taken with respect to the maximum temperature permissible, and devices which will promote a rapid rate of distillation are highly desirable adjuncts to the standing laboratory apparatus.

Figure 1 shows an extremely convenient and efficient stillhead that has been used for general concentration purposes in this laboratory during the past 4 years. When this is

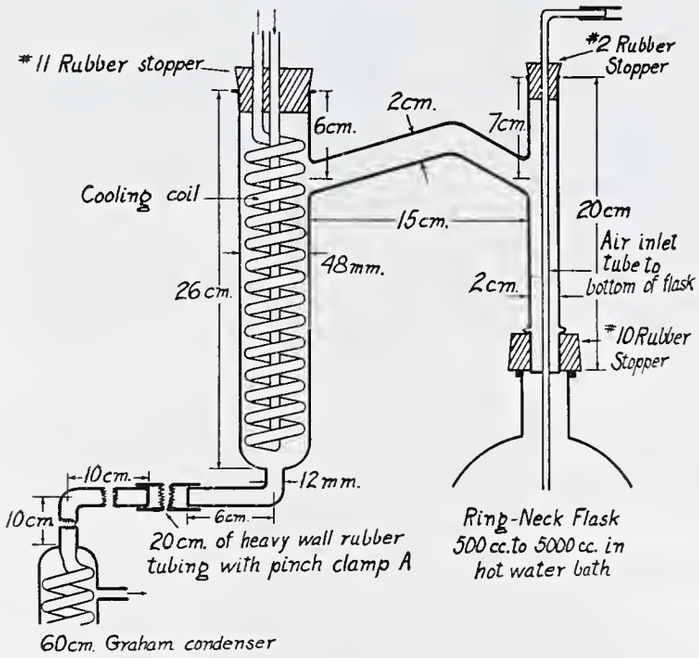

Figure 1

attached to a 5-liter flask, a distillation rate of 2 liters of water an hour can be maintained from solutions that do not froth badly, while from alcohol solutions the rate can easily be made to exceed 3 liters an hour. A similar apparatus, on a scale somewhat more than twice as large, and provided with a 5-liter bulb on the vapor tube, when attached to a Pfaudler steam-jacketed laboratory still, permits from 10 to 11 liters of water an hour to be distilled. The cooler coil in this apparatus is constructed of block-tin pipe, and a baffle plate is hung inside the bulb so as to intercept spurts of liquid from the still.

The dimensions given in the diagram are those of the stillheads set up in pairs on each workbench. The apparatus consists of a vapor tube constructed of 2-cm. tubing, furnished with a side arm of the same diameter, which is sealed into the wall of a cooling chamber 48 mm. in diameter. The cooling chamber contains a coil of about 14 turns of 8-mm. tubing suspended from the rubber stopper in the top. The advantage of the apparatus is the provision of relatively large-bore tubing to accommodate the hot expanded vapor, together with a cooling surface to reduce this volume and condense a part of the vapor, before it must pass through tubing of small size. The desirability of an arrangement constructed on this principle was first pointed out to the authors by H. A. Spoehr.

A number of heads of variously modified dimensions have been constructed—for example, a longer coil has been fitted into a correspondingly longer cooling chamber, or has been sealed to tubes passing through the wall of the cooling chamber. The most serious disadvantage of a longer coil, aside from its inconvenience, is the danger of fracture just below the rubber stopper when the flask must be shaken. A fused-in coil is more difficult to construct, but is necessary if the presence of rubber must be avoided.

The heads are suspended from an overhead bar by a length of brass chain which contains a spiral spring of the type used for bird cages; this flexible arrangement cares for the rise of the flask in the water bath as the load diminishes, and permits agitation of the flask by hand should this be necessary. The Graham condensers are likewise suspended from chains. These are placed at the end of the bench, or pass through holes cut to accommodate them, and are protected by being wrapped with a single layer of stiff wire gauze. Large filter flasks are employed as receivers; stopcocks in the vacuum line to each permit the stills to be used singly when desired. The supply of water to the cooling coils is controlled independently from that to the condensers.

To begin a distillation, screw pinchclamp *A* on the rubber connection between stillhead and condenser is closed, and the receiver is evacuated. The ring-neck flask is then placed in position in the hot-water bath with the air-inlet tube reaching to the bottom (this tube should not be constricted at the lower end), and the short length of rubber tube at the top is clamped. The neck of the flask is held firmly against the lower surface of the rubber stopper while pinchclamp *A* is opened. Water is admitted to the condenser, and a slow stream of air is allowed to flow through the air-inlet tube. After distillation has begun and any tendency of the solution to froth has subsided, water is admitted very gradually to the cooler coil. The rate of distillation immediately accelerates, and great care must be exercised with many solutions to prevent frothing over. Should this become imminent, the water supply to the cooler is immediately shut off and clamp *A* is closed. New supplies of solution may be added to the flask as needed through the air-inlet tube; when this is done, however, clamp *A* must be closed and the water supply to the cooler shut off. Alternatively, a short length of 2-mm. tubing through the stopper of the flask may be used, with proper connections, to admit a continuous slow stream of fresh solution.

Although primarily designed for the rapid distillation of large volumes of solutions, the stillhead is also advantageous when only small volumes are to be concentrated. The reversed rubber stopper permits the use of ring-neck flasks as small as 500 cc., and the less convenient side-neck distillation flasks are not required. This has many advantages when concentrating a solution previous to crystallization.

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Continuous Laboratory Topping Apparatus

H. T. Rall and H. M. Smith, U. S. Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

INVESTIGATIONS concerned with the character and composition of the less volatile constituents of petroleum should be conducted with material as little changed from the original as possible. This means that the more volatile components of a crude oil must be removed under such conditions that there is only a minimum opportunity for decomposition to occur. In several projects at this station there has been need for a continuous topping method that would remove gasoline, kerosene, and gas oil from petroleum without decomposition either of the tops or of the residuum. In two of these investigations (*1*, *2*) the gasoline was removed at 100° C. by distillation with natural gas, and the kerosene and gas-oil fractions were subsequently removed by steam distillation in a gas-fired still. However, this necessitates heating the oil to several hundred degrees Centigrade, and even with steam there is considerable possibility for decomposition where the oil is in contact with the hot still walls, particularly with certain types of crude oil. In connection with some work now under way, it seemed advisable to develop means of topping that would remove all of the lighter constituents up to oil having a viscosity of about 50 seconds Saybolt without heating the crude above 150° C. The fundamental principle used to accomplish this was that of isothermal evaporation from a thin, heated film of oil at pressures of 2 to 5 mm. of mercury. A few experiments indicated that, in addition, a short fractionating column and the sweeping action of a small stream of inert gas would help considerably in obtaining the desired objectives. The fractionating column virtually eliminated overlap between distillate and residuum, while the small gas stream, countercurrent to the oil flow, besides substantially reducing the effective evaporation pressure of the oil, continuously removed the more or less stagnant layer of heavy vapors formed by evaporation from the oil film.

Description of Apparatus

As a result of several experiments the apparatus shown in Figure 1 was developed. It consists essentially of two independent parts, the heating circuit and the topping system

The heat needed by the process is supplied by the hot vapors of a liquid boiling in the flask, *A*. These vapors ascend through line *B*, enter the outside chamber of isothermal heating unit *C* at the top, and pass through the chamber and out at the bottom to *D*, where they are condensed and returned to the boiler, completing the circuit for the heating medium. The temperature of the vapor leaving the bottom of the still is determined by thermometer *E*. In practice, the vapor stream should have a velocity and volume sufficient to maintain this temperature constant, whether or not the topping section is being used.

The topping system may be considered conveniently by following first the path of the crude oil through the apparatus and then the course of the gas and vapors. The crude oil to be topped is poured into storage flask *F* through strainer *G* and drawn by the vacuum in the system through line *H* and control cock *I* into degasser and foam breaker *J*. The crude then enters the top of the isothermal heating chamber *C* through stopcock *K* and dripper *L*. The heating chamber is simply an eight-bulb condenser; the four top bulbs are packed with No. 18 steel jack chain, and the four bottom bulbs are empty. The chain provides much surface and serves as a heat reservoir to heat the cool, incoming crude oil quickly. The oil passes downward through the still and eventually runs out of dripper *M* into topped-oil receiving flask *N*. By proper manipulation of stopcock *O*, flask *N* may be removed, emptied, and reëvacuated without stopping the distillation.

While the crude oil is flowing downward through the heater, a small stream of inert gas is admitted in the center of the bottom bulb at *P*. This gas rises countercurrent to the descending oil film and carries the vapors evaporated from the crude into fractionating tower *Q*, which is also packed with No. 18 jack chain. Here the heavier fractions of the distillates are separated and washed back, while the vapors pass to condenser *R* where they liquefy, the condensate collecting in the receiver, *S*. The gas passes through flask *S* and line *T* to the vacuum pump and thence to the atmosphere. It is essential that receiver *S* be kept cold enough so that the vapor pressure of the distillate will be negligible. For the same reason condenser *R* must be cold enough to liquefy all vapors.

The operating procedure is as follows:

The entire topping system is evacuated to a constant minimum pressure which should be 2 mm. or less.[1] Nitrogen or natural

[1] If the apparatus is absolutely free of leaks and of material having a measurable vapor pressure at the temperature of the manometer, the pressure indication should be zero. In practice these conditions are not completely fulfilled.

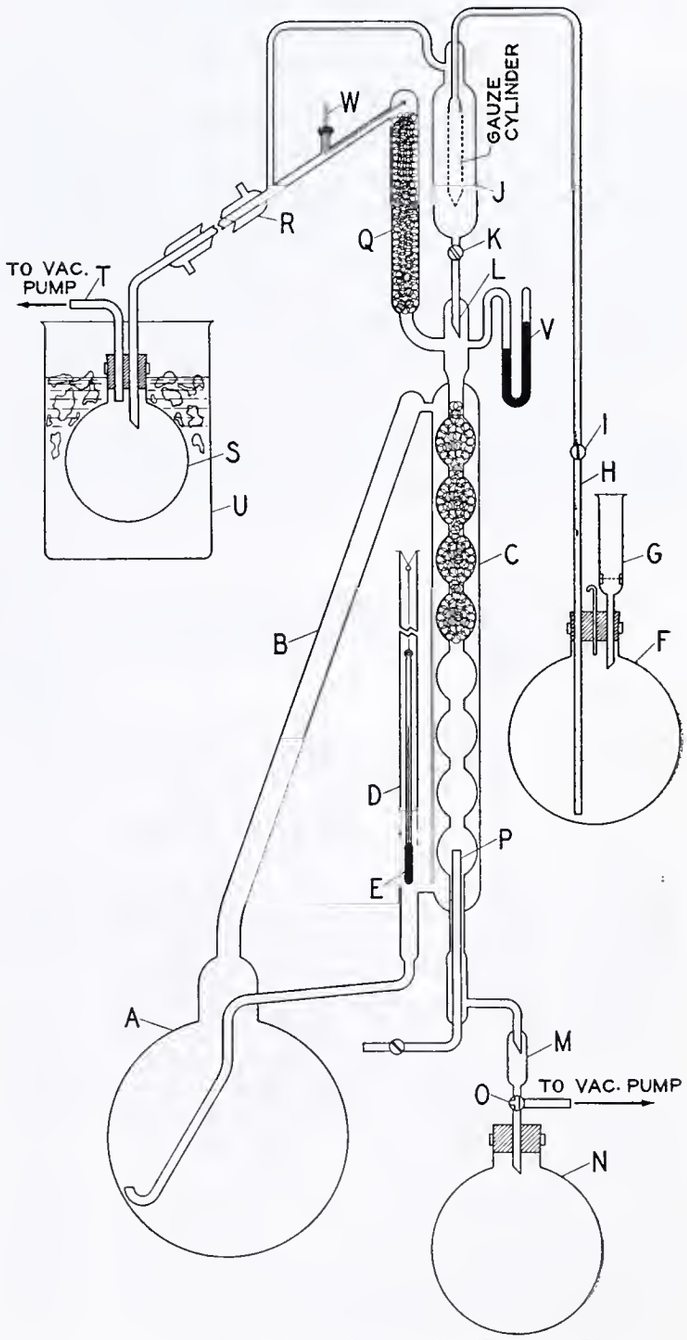

Figure 1. Isothermal Crude Oil Topping Unit

gas is then admitted until the manometer remains constant at the working pressure, generally 8 to 20 mm. of mercury, depending upon the extent of topping desired. This gas supply is easily controlled by a fine needle valve which has a constant pressure of one pound per square inch (0.07 kg. per sq. cm.) gage on the inlet side, so that in effect the needle valve acts as a flowmeter, and, once the initial evacuation pressure and working pressure have been fixed, there will be no fluctuation unless leaks develop. There will be small amounts of dissolved gas evolved from the crude, but, if the pump has ample capacity and the crude input to the degasser is kept reasonably constant, these gases will not

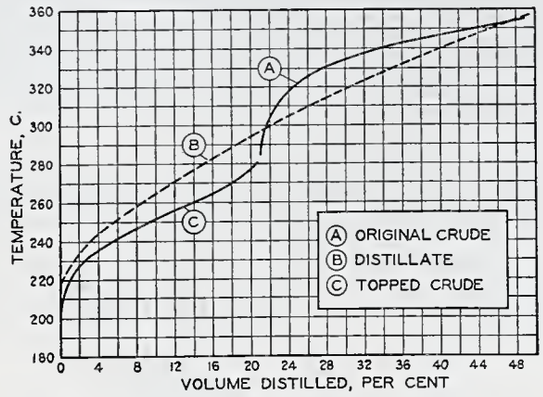

Figure 2. Engler Distillation Curves

appreciably affect the pressure. A flowmeter could be inserted advantageously in the gas supply line to afford visual evidence of the amount of gas entering. After a constant working pressure has been set, the crude is allowed to enter slowly until temperature equilibrium in the fractionating tower is attained, when the rate of crude input is fixed to maintain the desired temperature at the top of the fractionator, as indicated by the copper-constantan thermocouple, *W*. If the entire apparatus is well insulated, uniformly reproducible results should be possible since the following factors, which also control the reflux, are fixed: total and partial pressure, heat input, and crude input.

This apparatus has been used for topping a crude oil from the Port Neches Field, Texas. The characteristics of the original crude and of the topped oil, as indicated by vacuum distillation at 40 mm. pressure, are shown in Table I.

Table I. Vacuum Distillation at 40 mm. Pressure

	Original Crude	Topped Crude[a]
Initial temp., ° C.	114	194
Per cent distilled at 125° C.	1.35	0.0
150° C.	6.60	0.0
175° C.	15.70	0.0
200° C.	26.20	1.2
225° C.	35.75	11.5
250° C.	43.55	21.0

[a] Topped at 158° C. (boiling turpentine) and 19 mm. total pressure with about 16 mm. partial pressure of natural gas.

A four-unit apparatus has also been constructed, in which the units are connected in parallel to the crude-oil source, topped-oil receiver, gas inlet, distillate receiver, and vacuum pump. Topped oil from this apparatus, using nitrogen as the inert gas and a temperature of 158° C., shows virtually the same characteristics as that given in Table I. There is a small gap between the topped oil and the distillate, as shown in Figure 2, where distillation curves for the crude oil, topped oil, and distillate are given. These are all made with a standard Engler apparatus. The curves indicate that the separation is fairly sharp.

The apparatus described is very flexible from an operating standpoint. Liquids covering a wide range of boiling points may be used as the heating medium, and pressures may be varied over a considerable latitude. The partial pressures of the gas used may also be changed to suit conditions, as may the kind of gas used. It is obvious that the capacity of such an apparatus is small. The four-unit set-up has a capacity of 200 to 300 grams of topped oil per hour when used with the crude oil mentioned above under conditions removing about 21 per cent of the crude. The apparatus may be constructed readily from materials usually available in the laboratory.

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Determination of Phosgene by the Soda Method

Effect of Fire-Extinguisher Chlorinated Hydrocarbons

Maryan P. Matuszak,[1] U. S. Bureau of Mines, Pittsburgh, Pa.

It has been claimed (*6*) that values obtained by the U. S. Bureau of Mines with the alcoholic soda method (*2, 3*), for phosgene produced by oxidation of carbon tetrachloride, were too high because of "hydrolysis of carbon tetrachloride and other chlorinated hydrocarbons."

That no error due to the presence of carbon tetrachloride was found in blank determinations made under the specified conditions of analysis was confirmed by a tube experiment (*2*, Table III), in which three determinations showed no phosgene whatever, although a concentration of carbon tetrachloride of 14,000 p. p. m. was present. In several similar blank determinations the writer has likewise failed to detect any error due to absorption and saponification of carbon tetrachloride, even when using a more sensitive technic (*4*) in the Mohr titration than the earlier workers.

It is not implied that carbon tetrachloride cannot be saponified by alcoholic soda. But if the conditions of analysis used in the earlier work—absorption, at 0.5 liter per minute, of 4 or 5 liters of air containing carbon tetrachloride up to 5850 p. p. m., or of 0.5 to 1 liter containing up to 14,700 p. p. m., by a petticoat-bubbler absorber containing 50 cc. of *N* sodium hydroxide in 85 per cent alcohol—are maintained, and if neutralization is not unreasonably delayed, no error due to this compound is present.

Chloroform, the next most abundant component of commercial fire-extinguisher liquids, saponifies more readily than carbon tetrachloride (*5*). Hence, experiments were made to determine the concentration at which it causes a detectable error under the conditions of analysis.

Chloroform-containing air samples, 5.08 liters in volume, were absorbed by 50 cc. of *N* sodium hydroxide in 85 per cent alcohol in a petticoat-bubbler absorber during 10.5 minutes. The Mohr determinations were made with great care. Neutrali-

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zation was made to phenolphthalein with nitric acid, concentrated at first and 0.25 N near the end. Although no effort was made to hurry the work, neutralization was usually made within about 10 minutes after absorption. Heat liberated during neutralization was removed by cooling with tap water, to avoid decreasing the sensitivity of the chromate indicator. Then 1 cc. of M sodium bicarbonate was added, to insure a pH of about 9, and 1 cc. of 10 per cent potassium chromate.

Comparison of the titrated solution was made by reflected (not transmitted) yellowish light against a gray background with a freshly prepared reference solution containing similar amounts of reagents and a slight excess of sodium chloride. Some flasks of Pyrex glass made the yellow solution appear darker than others, an effect that appeared to be independent of wall-thickness; hence, the flasks used were matched to eliminate this effect. Titrations were continued until the reddish end point persisted for at least 5 minutes. This sometimes took 15 minutes or more, for although an apparently permanent end point was reached with the first 2 or 3 drops of 0.00818 N silver nitrate, a much larger volume could be added after several minutes. The data are given in Table I.

Table I. Absorption and Saponification of Chloroform

Chloroform	Apparent Phosgene	Chloroform	Apparent Phosgene
P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
1000	0	3990	43
1410	3	6410	89
1430	2	6780	92
1496	3	8170	113
1950	16	10920	153
2810	44	14500	196
2830	43	14600	190

Since, in the fire experiments (*2*, Table II), the concentration of fire-extinguisher liquids varied from 2000 to 5130 p. p. m. (calculated as carbon tetrachloride) and since only about 10 per cent of this was introduced as chloroform, no error due to absorption and saponification of this compound was present. Such error, even with the more sensitive titration technic, does not begin to appear until the chloroform concentration is at least twice the maximum introduced in the fire experiments.

In the tube experiments (*2*, Table IV) the initial concentration of chloroform was of the order of 1400 p. p. m. But, even if it all escaped decomposition or oxidation—which could scarcely have been true, as the total concentration of chlorinated hydrocarbons decreased by about 38 per cent—a detectable error was unlikely, as the air samples and the absorption periods were only one-fifth or one-tenth as large as those used in obtaining the data of Table I. Moreover, any possible error must have been negligible in comparison with the phosgene reported, 3700 to 3800 p. p. m.

Other experiments showed that Pyrene, a typical fire-extinguisher liquid (*2*, No. 1), was several times more resistant to saponification than chloroform, indicating that the values of 15 to 60 p. p. m. for phosgene found in fire-gases by the Bureau of Mines were not subject to any appreciable error because of chlorinated hydrocarbons introduced as fire-extinguisher liquids.

The alleged high soda values obtained by other workers (*6*) were probably due to insufficient removal of hydrogen chloride or precipitation of silver carbonate in the Mohr titration (*4*). The former appears to account for the only numerical data published in support of the alleged error, which were obtained with the unpurified gas from a toluene solution of phosgene and not with purified fire-gases; the latter, for the high values obtained in experiments on the thermal decomposition of mixtures containing carbon tetrachloride, for which no numerical data were published. Such error would be the more prominent the larger the air samples taken for analysis.

The soda method can be improved by acidifying with nitric acid and boiling out the carbon dioxide before neutralizing and titrating, and can also be rendered less objectionable by eliminating the use of alcohol. Aqueous N sodium hydroxide absorbs phosgene very effectively and is more stable and absorbs less chlorinated hydrocarbons.

The method of purification of fire-gases with zinc and mercuric sulfide (*1*) is preferable to the original method of purifying with silver nitrate and antimony trisulfide (*2*). The principal objection to the older method—that nitric acid, formed in the removal of hydrogen chloride by silver nitrate, reacts with antimony trisulfide to give hydrogen sulfide—is obviously inoperative if the gas is passed first over antimony trisulfide and then over silver nitrate, for any hydrogen sulfide formed by reaction of the former with hydrogen chloride is removed by the latter.

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A Distillation Apparatus for Phenols in Water

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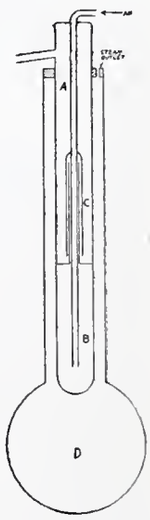
The apparatus illustrated was designed for the steam distillation of phenols from water solutions, and is simpler and more compact than the usual type. Instead of the box with a series of tubes and connections as described by Shaw (*1*), the outfit is condensed into a single unit.

This consists of a glass tube, A, divided into two compartments B and C. In part B is placed distilled water and in part C is placed the sample to be distilled. Through an inner tube fitting down into the lower compartment a slow stream of washed air is passed. The air becomes saturated with moisture and passing up is deflected down through the sample, releasing its moisture and maintaining a fairly constant volume. The tube is surrounded by a glass jacket. Steam, generated in flask D, passes up around the tube and escapes at the top, maintaining the temperature for distillation of the sample. The phenols present are thus distilled over and are condensed and collected in a graduated cylinder. Connections with which the vapors come in contact are made by means of ground-glass stoppers. No rubber tubes or stoppers are used, thus eliminating any possible contamination.



Any suitable indicator may be used to ascertain the amount of phenol in the distillate.

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The Tonometer

Study of Color and Brightness of White Films

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A STUDY of the paint and enamel films commonly referred to as whites reveals that very few can be classified spectrophotometrically as nonselective, and among those which are nonselective none reflect 100 per cent of the light. In other words, these opaque surfaces generally either contain coloring matter or are gray with respect to pure white. In fact, those who manufacture or use white coatings frequently complain that there are more significant visual color and brightness differences among commercial whites than among any common group of full colors.

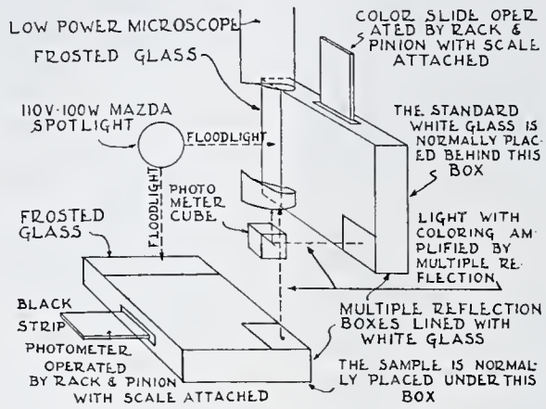

Figure 1. Diagram of Tonometer

These small variations in color are of more importance than is generally recognized. The question of whether a white is pleasing to the eye often depends on small traces of unsuspected color, and in the manufacture of quality white coatings a close control of color is both necessary and difficult. In addition, all organic coatings change slowly in color on aging, and the nature and amount of these changes frequently measure the practical value of the coating.

In dealing with whites, the three factors of major importance are brightness or total reflection, the hue toward which the sample deviates from pure white, and the extent of this deviation. This latter, which is the most important, might be called depth of tint, but Ridgway (*5*) has spoken of the graduations between a full color and white or black as "tone," and the term is used in that sense in this paper.

Tremendous strides have been made in the last few years in developing machines for measuring color, but a survey of the instruments on the market and of the literature (*1*, *4*) has failed to disclose a thoroughly satisfactory machine for the so-called white field. Instruments for measuring brightness are available, but they do not satisfactorily measure color. The ordinary color analyzer, which measures the relative intensity of the reflected light at various wave lengths, is not sufficiently practical in the region approaching white, because the variation in the intensity between different wave lengths is small compared with the total intensity at all wave lengths. Instruments, such as the Pfund tintometer (manufactured by the Munsell Color Company), fail to allow for important hue variations.

Fortunately, the problem of measuring the color of commercial whites is simplified by the fact that the deviation from pure white is almost always toward some member of the yellow family, or toward the complementary blues which are added to neutralize the yellow color of all common organic vehicles. The problem in its simplest form consists therefore of measuring the yellowness or blueness of these white coatings. Based on this principle, the Pfund tintometer measures the yellowness of the coating by measuring the amount of blue glass which must be inserted into the reflection from the sample to neutralize the yellow present. The accuracy is greatly increased by using the principle of multiple reflection to intensify the tone to the point where it can be accurately measured. Difficulty is encountered in securing a permanent blue glass which is the true complement of yellow, and no allowance is made for the fact that hue variations in the yellow present have an important bearing on the appearance of the white. In spite of these disadvantages, it is felt that the Pfund instrument has greater merit for the purposes under consideration than any of the color instruments examined.

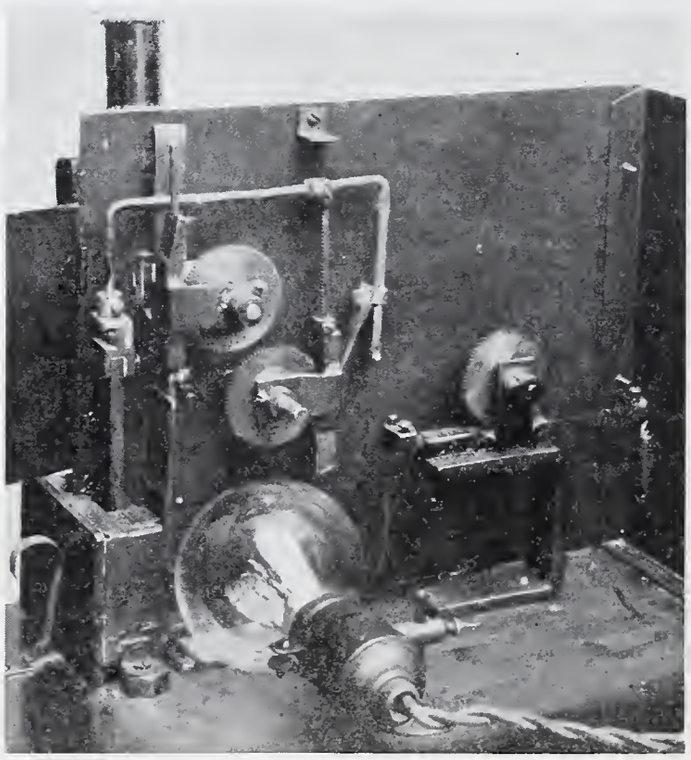

Figure 2. Tonometer with Back and One Side of Housing Removed

Racks and pinions control movements of black-strip photometer, color slides, and auxiliary shutter over upper reflecting box. Projecting into top of reflecting box is one of color slides. Other reflecting box is directly beneath lamp.

The instrument described in this paper utilizes the multiple-reflection principle of the Pfund tintometer, but measures normally the amount of yellow glass which must be inserted into the reflection from a standard white to match the color of the sample. Standard yellow glasses of good color permanence have been secured in graded steps to cover the range of yellow hues commonly encountered in white coatings. This includes the range from green-yellow to red-yellow. This instrument has been designed for practical use in the ordinary control or research laboratory. It is simple in

design and operation; is relatively inexpensive to construct; requires only a short time for each reading; and gives almost no bleaching of the sample during the test. The readings have a direct significance and permit easy visualization of color differences from an inspection of tabulated data.

In use for the last six months, the instrument has proved of value in connection with a number of important problems. It has been used to maintain a constant standard in controlling the production of certain products, where both dry plate and wet standards have a tendency to drift. It has been used to study the effect of film thickness and baking conditions on color, and has proved invaluable in following the changes in color which take place during the aging of white coatings under various conditions of exposure.

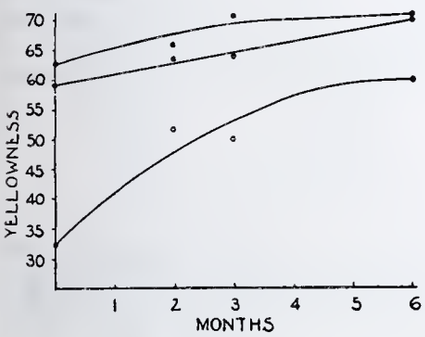

Figure 3. Yellowing of White Air-Dry Enamels Exposed to Diffused Light

Apparatus and Method

Some of the instruments for measuring color, such as the Razek-Mulder (*2*), the Keuffel and Esser (*3*), and the Pfund, have means for amplifying color differences either by scale readings or appearance of actual color. In developing the tonometer, account was taken of these two types of amplification. Scale amplification is a simple mechanical problem. Color amplification is accomplished by the use of multiple reflection boxes. The instrument is self-contained and mounted on a base-board 19.25 inches long and 10 inches wide. Its working parts are built in and around a housing of aluminum 11 inches long, 8.75 inches high, and 6 inches deep. It should be possible to construct the instrument in the average plant shop for less than $200. A diagrammatic representation is shown in Figure 1.

Two boxes, each 2 inches wide, 3 inches long, and 1 inch deep, are used to obtain the degree of multiple reflection desired. These boxes are lined with an opal glass far enough on the blue side of theoretical white, so that the majority of readings are in one direction from this arbitrarily selected glass standard. The openings through which the light enters are covered with diffusing glass in order to obtain even diffusion of light. The boxes are illuminated by a 110-volt, 100-watt Mazda spotlight. The light emerges from the end opposite the light entrance and the two fields are brought into juxtaposition by means of a photometer cube. The combined fields are then viewed through a lens system, a low-power microscope being used in the present assembly.

A slot is cut in one side of the upper reflecting box, as indicated. A color slide is introduced through this slot to vary the yellowness of the light which is directed into the eyepiece. The opal glass covering one 2 × 3 inch side of each box is easily removable to permit substitution of a sample to be measured. Normally, commercial whites are on the yellow side of the arbitrary standard, and the sample then is placed over the box opposite that in which the color slide is used. Employing this procedure, it will be seen that the instrument is a color synthesizer rather than a color analyzer.

Obviously, as a color slide is introduced into one of the fields, the brightness of that field is reduced, making a color depth (saturation) match difficult. To compensate for this undesirable feature, a slot, similar to the one through which the color slide is operated, is cut in one side of the other box through which a black strip may be introduced to equalize the brightness of the two fields while obtaining the color match. This black strip may be used, with the color slide removed, for making actual brightness determinations. A difficulty arises, however, in that the eye is not capable of entirely eliminating the effect of color differences when attempting to compare brightness. To obviate this, a green glass is placed over the photometer cube, thus covering both fields. Green successfully masks color differences in the normal range of hues encountered. It is not satisfactory for the purples, but these hues seldom occur in commercial whites.

Both color slide and black strip are attached to racks and pinions for convenience of operation. Scales are attached to these racks and pinions, so that quantitative measurements of color depth and brightness may be recorded. The scales are divided into arbitrary units of such magnitude that, when taking into account the degree of multiple reflection employed, the least significant figures represent differences slightly greater than the average eye is able to detect.

The opal glass standard is checked against magnesium oxide, the accepted standard for whiteness. The magnesium oxide is applied to a flat surface (a piece of the white glass is suitable) by burning magnesium ribbon and allowing the oxide to condense on the surface. After a coat about 0.002 inch in thickness is obtained, a reading for color should yield a value of 39.3 Y, indicating that the opal glass is 39.3 points on the blue side of pure white. The "black-strip" photometer is checked at the same time and should yield a value of +67.5, indicating that the opal glass is 67.5 points on the gray side of pure white. Table I is a typical set of calibration readings.

Table I. Calibration of White Glass *vs.* Magnesium Oxide

	Color 4		Brightness	
	First operator	Second operator	First operator	Second operator
Magnesium oxide	40 Y	38 Y	+67	+71
Magnesium oxide check	40 Y	39 Y	+67	+65
Magnesium oxide check	38 Y	42 Y	+68	+68
Magnesium oxide check	40 Y	41 Y	+67	+69
Magnesium oxide check	38 Y	39 Y	+66	+67
Magnesium oxide check	38 Y	39 Y	+67	+68
Average	39 Y	39.7 Y	+67	+68

The color slides vary from green-yellow to red-yellow. Each slide is cut so that a sample will yield essentially the same yellowness reading with the two slides closest to it in hue, thus indicating that all slides have for practical purposes the same yellow saturation. Five slides are in use at present, selected on the basis of practical experiments. These slides are numbered, the greenest yellow being No. 1 and the reddest yellow No. 5. Table II shows some of the results from which the final series was selected.

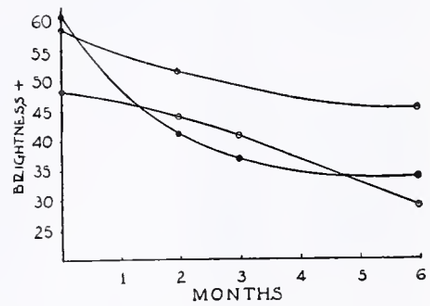

Figure 4. Brightness of White Air-Dry Enamels Exposed to Diffused Light

Table II. Calibration Values for Selection of Color Slide Series

Film	Yellow Glass	Yellowness
Excessive red tone	4	84 Y
	5	84 Y (best match)
Red tone	3	60 Y
	4	55 Y (best match)
	5	55 Y
Natural white	1	84 Y (best match)
	2	84 Y
Natural white	1	83 Y (best match)
	2	82 Y
Blue tone	1	65 B (best match)
	2	65 B
Badly yellowed panel (slight red tone)	1	106 Y (best match)
	2	110 Y
	3	104 Y

One bulb (Figure 2) illuminates both reflecting boxes. Any variation in light intensity is therefore equalized in both fields. The lamp is attached to a post by means of a set screw, and may be moved in a vertical direction or a

horizontal circular motion. This permits flexibility in establishing the position of the lamp, which gives the best match when the standard opal glass is placed over both fields.

An actual determination ordinarily requires but a few minutes. If the sample is yellower than the standard opal glass, it is placed over the reflecting box opposite the one in which the color slide is introduced. If it is bluer than the standard, it is placed over the box in which the color slide is used. Having properly placed the sample, a color slide is attached and run into the field. If the hue is not right—e. g., if it is too red—a color slide less red in hue is tried. With relatively little experience, the correct slide can be quickly selected. With this slide in position, its depth in the field is varied, at the same time adjusting the brightness with the photometer. When a match is obtained, the reading on the color scale is observed. When the sample is yellower than standard, the letter Y is used in connection with the numercial value, and when it is bluer the letter B is used. In addition, the number of the color slide employed is recorded, and indicates the hue position in the color slide series. An example of a recorded measurement is Color (No. 3), 62 Y.

Now, by removing the color slide from the field and placing the green glass over the photometer cube, a brightness measurement may be made. If the sample is brighter than the standard, it is placed over the box in which the black strip is employed, or, if less bright than the standard, over the other box. The photometer is now adjusted until a match is obtained. If brighter than standard, the plus sign is used with the numerical value, and if less bright than standard, the minus sign is used. An example of a recorded measurement is Brightness, +45. At least three readings each for color and brightness must be made and averaged for final results.

In practically all cases, films which are yellower than the opal glass are also brighter. In rare instances, however, a yellower but less bright film is encountered, which is difficult to handle in that, while obtaining the color measurement, the black strip cannot be used for equalizing brightness. For this purpose a sliding shutter, attached above the light entrance to the box in which the color slide is used, may be employed to equalize brightness.

Discussion of Results

In studying various white air-dry enamels exposed in diffused light, over a period of six months, the color results shown in Figure 3 were obtained and show at a glance the comparative rates of yellowing. Perhaps the most significant factor shown here is that the enamel which was initially much whiter than the others in six months yellowed into the same range as the others. By actual computation of time, these readings, twenty-seven in number (three for each point), required less than one-half hour. To have made comparisons at periodic intervals against freshly prepared control panels would have required much tedious work and would have been limited in value by possible color changes in the can during aging. Brightness measurements, shown in Figure 4, indicate a gradual graying on aging in all cases, although the rate of graying varies considerably.

Table III. Effect of Temperature Variations on Color and Brightness

	Temperature of Bake ° F.	Color (Slide 3)	Brightness
1	258	48.3 Y	+40.3
	263	51.6 Y	+37.3
2	258	53.8 Y	+34.3
	261	55.2 Y	+44.6
3	258	48.0 Y	+47.6
	263	49.6 Y	+40.8

Another series, represented by Figure 5, was designed to measure the changes which occur in white baking enamels during the first few days of exposure. The exposures were outdoors, diffused light, and dark. Practically no change is noted in the panel exposed in the dark, appreciable bleaching and then gradual yellowing is seen in the diffused light exposures, and rapid bleaching and then fairly rapid yellowing in the outdoor exposure. Brightness measurements during this period show no appreciable change.

The instrument has also been used to detect the effect of temperature variations in baking, as shown in Table III.

Valuable data are being obtained upon color and brightness changes in the can upon aging. Two blued whites yielded the results shown in Table IV. These variations represent very appreciable differences to the unaided eye and appear of especial importance in the control of production.

Table IV. Color Brightness Changes during Can Storage

	Color (Slide 1)	Brightness
Initial	24.5 B	+30.3
1 month	0.0	+31.0
Initial	70.0 B	−52.6
3 months	56.0 B	−44.0

Finally, the instrument can be used to good advantage in studying and guarding against variations in methods of film application. For example, two heavy coats of a blued

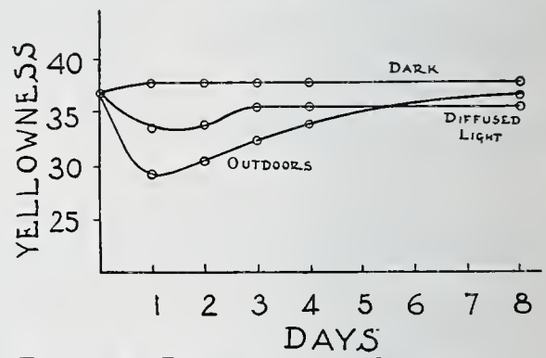

Figure 5. Bleaching and Yellowing of White Air-Dry Enamels during Initial Stages of Exposure

enamel sprayed on steel yielded the readings 15 Y and +40. One coat on steel gave readings of 40 B and −20. The film thickness of the two coats was 0.005 inch and of the one coat 0.0013 inch.

Differences in gloss apparently do not affect the readings for color and brightness. This has been checked by lightly sand-blasting a piece of the white glass used as standard and comparing it with a piece of the glass as normally employed. This comparison, representing a wide difference in gloss, revealed no significant differences in color and brightness.

Summary

There is need for a more practical color instrument designed primarily for the measurement of yellowness in white films, which will yield approximate general hue matches, and which can also be used for brightness measurements. Such an instrument must offer a direct, rapid, and accurate method; must be extremely simple to operate; must yield results which are of immediate practical significance; and must be relatively inexpensive to construct. The instrument which is described may be used for studying the initial yellowness and brightness of white coatings and for classifying them with respect to other hues which may be present; for the study of film aging with respect to these properties; for determining the effect of temperature variation; for determining can stability with regard to yellowness and brightness; and for measuring the effect of variations in film application, due particularly to differences in film thickness.

Acknowledgment

Acknowledgment is made to C. F. Rassweiler and H. H. Hopkins for helpful suggestions and to J. B. Gregor for assistance in calibration and development of data.

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Nickel Microbomb for Microestimation of Organic Arsenic

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VARIOUS macrofusion methods for the determination of organic arsenic have been proposed from time to time, most of which may be roughly divided into two classes: In the one decomposition is brought about by wet methods and in the other the compound is subjected to a dry fusion in an open crucible. Many of these procedures are not only tedious of operation, but cannot be applied to compounds such as cacodylic acid which are difficult to decompose.

St. Warunis (*5*) fused the organic compounds with sodium peroxide and sodium nitrate in a nickel crucible, and determined the arsenic as magnesium pyroarsenate. Pringsheim (*4*) used sodium peroxide and a silver crucible, determining the arsenic as the pyroarsenate. Parr (*2*) determined the arsenic in inorganic substances by means of a sodium peroxide explosion using a bomb, but he does not state in detail the method used.

It was decided to determine whether or not a sodium peroxide–sugar explosion in a microbomb could be used to convert organic arsenic completely to sodium arsenate, and also whether the delay of a subsequent precipitation could be avoided. The steel bomb described by the author (*1*) was at first tried. A precipitation of arsenic was found necessary because of the presence of iron and chromium in the products of corrosion from the steel cup. The method then became lengthy and offered no advantage over present micromethods.

In order to avoid this complication the nickel cup was made, as described (*1*). The lock used was made similar to that provided as standard equipment for the standard macro sulfur bomb. A handle, designed for removing the cap, facilitates manipulation. The amount of corrosion was much less than that obtained from the steel cup, and proved to have no effect on the direct titration against the iodine liberated from potassium iodide by the sodium arsenate formed.

PROCEDURE

Place 20 to 25 mg. of sucrose, measured by means of a scoop constructed for the purpose, in the bomb and add the weighed sample, which is adjusted to contain about 1.5 to 3 mg. of arsenic. Add approximately 1 gram of sodium peroxide, also measured by means of a scoop. Place the lid on the cup, taking care that a nonpitted gasket is in place. Mix the charge thoroughly by shaking the bomb violently for at least 2 minutes. Tap the bomb on the table several times to insure that the charge is all in the bottom of the cup. Ignite by heating in the tip of a small hot flame for 35 to 40 seconds. Allow the bomb to stand in the air for 5 seconds and then cool and rinse it by immersing in cold distilled water.

Remove the lid from the bomb, washing it off into a Pyrex tube of 35-mm. inside diameter and 155-mm. inside length. Add almost enough water to cover the cup, which has been placed on its side in the bottom of the test tube, and warm to bring about the solution of the fusion. When the fusion is dissolved remove the cup by means of a looped nickel wire and rinse it with hot water.

At this time the volume of the liquid should be about 25 to 30 cc. Boil the solution in the test tube by means of a low flame from a microburner. A few glass beads aid in preventing bumping. The boiling should be continued until the volume has been reduced to about 10 cc. This also insures the removal of hydrogen peroxide. Cool the solution and add 12 cc. of 12 *N* hydrochloric acid which has been previously freed from chlorine and dissolved oxygen by boiling for 2 minutes as recommended by Pregl (*3*). Cool the solution to room temperature by placing the tube in a water bath. Add 1 cc. of freshly prepared 10 per cent potassium iodide solution, allow the solution to stand for exactly 3 minutes, and then titrate with 0.01 *N* sodium thiosulfate solution until only a faint yellow color remains. Add 3 drops of freshly prepared 1 per cent starch solution and titrate to the usual end point. The color should not return for at least 5 minutes, but may become darker on prolonged exposure to the air. A blank, determined for the reagents being used, should be deducted. The blank is quite consistent and should not amount to more than 0.3 cc.

The method was found to apply over a range of typical organic arsenic compounds, and Table I shows a few of the results obtained on some of the compounds employed.

TABLE I. ARSENIC CONTENT OF COMPOUNDS ANALYZED

Substance	Weight of Sample	Arsenic: Calculated	Arsenic: Determined	Arsenic: Pregl standard micromethod
	Mg.	%	%	%
Butylarsonic acid	6.855	41.17	41.35	41.16
	6.540		41.38	41.31
	6.225		41.45	41.30
	5.760		41.50	...
Cacodylic acid	4.585	54.26	54.18	54.04
	5.019		54.12	54.31
	4.979		53.98	...
	4.693		54.09	...
Phenylarsonic acid	5.925	37.10	36.93	36.64
	7.925		36.51	36.96
	4.705		36.64	36.72
	5.635		36.95	...
Triphenylarsine	9.716	24.49	24.44	24.35
	11.918		24.43	24.42
	11.624		24.43	...
	11.464		24.55	...
Sodium-*p*-hydroxyphenylarsonic acid	9.550	28.61	29.95	29.83
	7.258		30.04	29.62
	9.825		29.88	...
	9.705		29.85	...

This method was found to be equally effective with semimicrosamples (Table II).

TABLE II. ARSENIC CONTENT OF COMPOUNDS ANALYZED USING SEMI-MICROSAMPLES

Substance	Weight of Sample	Arsenic: Calculated	Arsenic: Semi-micro	Arsenic: Pregl standard micromethod
	Mg.	%	%	%
Triphenylarsine	22.254	24.49	24.47	24.35
	19.375		24.51	24.42
	18.996		24.33	...
Cacodylic acid	12.370	54.26	53.91	54.04
	8.447		54.14	54.31
	7.027		54.17	...

The procedure employed is similar to that given above. The amount of sodium peroxide should be increased to 1.5 grams, the volume reduced to 15 cc., and 15 cc. of hydrochloric acid added.

Before titrating, 3 cc. of 10 per cent potassium iodide are added and the customary 3 minutes allowed to elapse. The titration is then carried out as above, using 0.03 N sodium thiosulfate. It will not be necessary for all operators to use starch in detecting this end point.

The 0.01 N sodium thiosulfate solution is standardized by means of pure arsenious oxide, treating from 2.5 to 3.5 mg. A blank should be run and deducted.

In order to check the arsenic factor thus obtained, the sodium thiosulfate was also titrated against resublimed iodine and against the iodine liberated from potassium iodide by potassium iodate. The three factors obtained checked within experimental error.

Summary

The arsenic content of organic compounds may be determined by means of a sodium peroxide–sugar explosion in a nickel microbomb much more rapidly than by existing micromethods and with the same degree of accuracy. A duplicate determination, including the weighings and final titrations, may be made in 50 minutes.

Acknowledgment

The authors are indebted to H. E. Woodward and F. Bremner who checked the analyses using the standard micromethod of Pregl (*3*).

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Removal of Samples of Oil from Oil-Impregnated Paper

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When oil and paper high-voltage cable insulation is subjected to conditions of service or to laboratory treatments simulating such conditions, certain definite changes frequently take place in the oil. In order to investigate these changes, it is necessary to remove the oil from the paper without contaminating the oil. Extraction methods have been found to interfere with the viscosity and hydrophil tests (*2, 4*) used by this company. As is well known, the removal of the last traces of solvent from a heavy oil is a difficult and uncertain process. Since the viscosity of a system of two components of widely differing viscosities is greatly changed by small variations in the concentration of the component of lower viscosity (*1*), efforts to follow chemical changes in oils by means of viscosity measurements are partially invalidated by the presence of variable traces of solvent. Another objection to the use of a solvent is that in addition to removing the oil from the paper, it may remove certain substances which are not soluble in the oil and which are not wanted in the specimen obtained, as, for instance, natural resins. In such cases the values obtained by using the hydrophil test to measure the extent of oxidation are too high.

In order to avoid these errors, several mechanical methods, other than those requiring the use of solvents, have been tried in this company. It was recognized that the oil obtained by such methods might not be entirely representative of the total oil in the paper, owing to the selective adsorption by the paper of some of the impurities present. While the matter has not been investigated thoroughly, the work done here indicates that the magnitude of such errors is small as compared with those due to the use of a solvent. In the first two mechanical methods tried, both of which involved pressing the oil from the paper, difficulty was experienced in obtaining the oil free from fine paper fibers which interfere with viscosity measurements and in obtaining sufficiently large samples of oil from tapes of relatively low oil content.

A centrifuge method, that is rapid as well as effective, has been found to eliminate the difficulties enumerated.

The apparatus is shown in Figure 1. Except as otherwise indicated, all measurements are outside dimensions.

In use, a tape from which oil is to be removed is wound on the reel, A. After the reel has been reversed a few times to loosen the winding, the roll is pushed off the shaft by means of the sliding guide and is placed in the funnel with the axis of the roll parallel to that of the funnel, as shown. The wide end of the funnel is then covered with a rubber cap to prevent air from circulating through the apparatus during the centrifugalizing process. The apparatus is assembled by dropping into the centrifuge tube, in the order given, the lower mounting complete with vial, the upper mounting, and finally the loaded funnel, the stem of which projects just inside the mouth of the vial.

The length of time and the speed required to centrifugalize most of the oil from the tapes vary, of course, with the nature of the samples. Often a 20-minute period at about 2000 r. p. m. suffices. By continuing the process, so much oil may be removed that the paper is

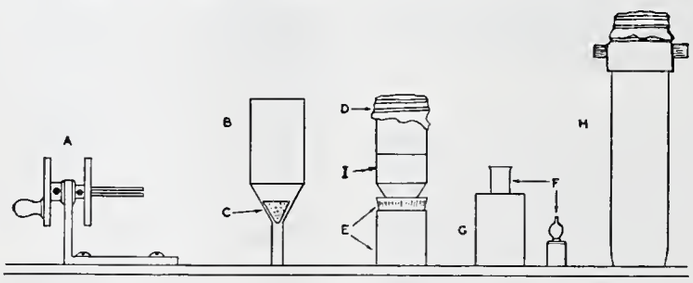

Figure 1. Apparatus for Removing Oil from Paper by Centrifugalizing

A. Reel with slotted shaft and sliding guide
B. Pyrex funnel. Body, including taper: 90 mm. long × 38 mm. diameter, stem angle 58°. Stem 30 mm. long, 7 mm. diameter
C. Platinum filtering cone, angle 60°
D. Rubber cap
E. Upper mounting: aluminum cylinder 39 mm. long × 38 mm. diameter, 6 mm. wall. Top 12 mm. beveled on inside to 1 mm. thickness to support rubber ring which fits both cylinder and shoulder of funnel
F. Weighing vial with glass stopper
G. Lower mounting: aluminum cylinder 52 mm. long × 38 mm. diameter × 3 mm. wall. Cylinder holds two gum rubber stoppers, the upper bored to fit vial *F*
H. Assembly complete in centrifuge tube 137 mm. long × 39 mm. inside diameter
I. Roll of impregnated sample in tube

no longer translucent but is opaque. Even when a longer period is required, the time consumed is not considered excessive.

Unless fine suspended matter is present in the oil in the paper, the sample obtained by the method is clear and free from sediment. The use of the filtering cone is recommended for straining out cable wax or bits of torn paper. Paper fibers do not seem to be dislodged during centrifugalizing.

Not only is the method satisfactory for ordinary samples, but it has also been found to be applicable to samples containing abnormally low quantities of very viscous oils. Since the oil is deposited in a small weighing vial, it can be weighed for test and used without loss.

As has been intimated, one of the reasons the device was designed was to obtain oil for viscosity tests. That the viscosity of the oil taken from radial samples of aged cable varies was observed in the investigations in this company. The possible significance of this phenomenon as regards electric transmission cable life in service is reported in the literature (*3*).

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Received May 14, 1934. This work forms part of a general research on the deterioration of high tension underground cable being undertaken by The Detroit Edison Company.

ter Meulen Method for Direct Determination of Oxygen in Organic Compounds Containing Nitrogen

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It has been shown recently (*3*) that when certain modifications are employed, the ter Meulen method for the direct determination of oxygen in organic combination yields very satisfactory results in the case of compounds containing carbon, hydrogen, and oxygen. By using a very active, thoria-promoted nickel catalyst, all the oxygen in the organic compound was converted to water which was completely retained by the first calcium chloride tube of the absorption train, since no oxides of carbon escaped methanation. Under such conditions the analysis of organic compounds also containing nitrogen should yield hydrogen, hydrocarbons, nitrogen, water, and ammonia. Since calcium chloride absorbs ammonia to a certain extent, ter Meulen (*1*) has proposed the use of a special tube carrying a charge of standard acid and in a second compartment calcium chloride. Any ammonia evolved during analysis is retained by the acid which is back-titrated at the end of the run. Thus the gain in weight of the tube due to ammonia can be evaluated and the water absorbed ascertained by difference. It appeared to the authors that in the absence of oxides of carbon in the effluent gases, procedure might be considerably simplified if an efficient water absorbent could be found which would not absorb ammonia. Reagent-grade sodium hydroxide in pellet form proved to meet these requirements. Pellets are to be preferred to a more finely divided form because they offer little chance for mechanical retention of ammonia.

Apparatus and Method

The apparatus previously described elsewhere (*3*) can be used without modification other than the replacement of all calcium chloride and ascarite with pellets of reagent-grade sodium hydroxide. A 5-inch (12.5-cm.) Schwartz tube charged with this sodium hydroxide served to retain completely the water corresponding to the oxygen in the sample. A second and third tube similarly charged, to act as guard tubes, complete the absorption train.

The method of analysis is identical with that already described (*3*), except that for compounds containing much nitrogen the time for an analysis may well be extended to 1.25 or 1.5 hours, in order to allow ample time for sweeping ammonia from the system. A relatively large amount of catalyst—5 to 10 grams—is desirable to prevent the appearance of oxides of carbon in the effluent gases to be absorbed by the sodium hydroxide. Such an amount of active catalyst gives persistent blanks. Thus the blank per half hour may be as high as 2 mg. with a freshly prepared catalyst. The initial blank gradually decreases with continued use of the catalyst to a few tenths of a milligram, owing to the slow reduction of the last traces of nickel oxide. Therefore, the values of these blanks must be carefully ascertained and used to correct the results obtained. In case there is a difference between the blanks determined before and after an analysis, the average blank is best employed.

Table I. Results of Analyses by Modified ter Meulen Method

Substance	Weight of Sample	Temperature of Catalyst	Oxygen Found	Oxygen Calculated	Nitrogen Converted to NH_3
	Gram	° *C.*	%	%	%
Acetamide	0.20685	350	27.14	27.10	85
	0.1910	350	27.14		58
Dimethylglyoxime	0.18615	350	27.50	27.57	45
	0.2117	350	27.61		53
Urea	0.1939	300	26.59	26.65	33
	0.1497	350	26.71		
3,5-Dinitrobenzoic acid	0.1596	350	45.11	45.27	60
	0.2010	350	45.22		
p-Nitroacetanilide	0.20745	350	26.70	26.66	58
	0.1946	350	26.88		
p-Nitrobenzeneazo-resorcinol	0.2295	350	24.53	24.70	54
	0.2337	350	24.61		

Results

The results of analyses made upon high-grade organic chemicals containing nitrogen, with sodium hydroxide employed as absorbent, are given in Table I. In addition to the oxygen content found, the percentage of the calculated nitrogen appearing in the exit gases as ammonia is also given. Although over 50 per cent of the nitrogen frequently appears as ammonia, it is improbable that a simultaneous de-

termination of oxygen and nitrogen (as ammonia) can be arranged because of the activity of the cracking surface in liberating nitrogen in difficultly reducible form, probably as free nitrogen, from the compounds studied. More stable nitrogenous compounds may prove an exception, since Smith and West (*4*), who have obtained excellent results in the nitrogen analysis of organic compounds containing nitrogen in the ring, and also of nitrogen derivatives of chaulmoogric acid by catalytic hydrogenation (*2*), have found it desirable to preheat strongly the gases evolved from the heated sample before passing them over the nickel catalyst. It is proposed to study this situation further.

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Identification of Common Glycosides

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WHEREAS many individual tests for the glycosides are found in the literature, hitherto they have not been applied to all glycosides and no systematic method for their identification has been available. The authors have found that known reactions, modifications of known reactions, and new color reactions with simple reagents will enable one to identify the more common glycosides.

The glycosides in Table I are best identified in the order given. (Picrotoxin, a compound closely related to the glycosides, is included in this study.) In all cases a few milligrams of each are treated at room temperature for about 2 hours with the reagents shown in Table II, so that effects of all reagents used on these glycosides are now determined and disclosed.

(For various confirmatory tests, see especially Merck's Reagenzien Verzeichnis, 1924.)

Table I. Identifications

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*		*k*	*l*
Phlorhizin	+	garnet	–	–	Br	Y	Y	Y	yR	Y	–	ltY, Or, rBr
Arbutin	–	Bl	–	–	Br	Y	BrG	Or	Y	Y	–	Or, BrBk
Digitonin	–	–	+	–	Y	Br	–	–	Y	Y	–	–
Picrotoxin	–	–	–	+	Y	Y	–	–	Br	–	–	Y, Or
Colocynthin	–	–	–	+	Cr	rBr	yBr	Y	BrR	ltY	Y	gold Y
Scillitoxin	–	–	–	+	brBk	Br	Br	Or	brG	Br	P	rBr
Amygdalin	–	–	–	–	dkG	Ca	–	–	–	–	–	Ca
Salicin	–	–	–	–	brR	Cr	Ca	Y	R	–	–	Cr, dkR
Strophanthin	–	–	–	–	brBk	G	Y	–	rBr	Br	Y	Br, brBk
Digitalin	–	–	–	–	Blood R	rBr	chR	–	R	P	Y	chR, dkR
Convallarin	–	–	–	–	dkBr	rBr	Y	pink	R	R	P	Y, Or, Br
Saponin	–	–	–	–	Br	rBr	–	–	Ca	R	–	ltY, orR, dkbrR
Sapotoxin	–	–	–	–	Br	rBr	pink	–	rY	V	Y	ltY, orR
Convallamarin	–	–	–	–	brY	rBr	pink	–	yBr	R	P	or, Br
Absinthin	–	–	–	–	–	Y	–	Y	rBr	brY	–	–

Bl = blue Ca = carmine G = green R = red
Bk = black Cr = crimson Or = orange V = violet
Br = brown Ch = cherry P = purple Y = yellow
Small letters = lighter shades; dk = dark; lt = light; comma = changing to

Table II. Reagents

	Reagent	Solvent	Per Cent of Reagent	Literature	Remarks
a	HIO_3	Dil. AcOH	1 to 5	(*4*)	Phlorhizin dyes silk yellow to blood red
b	$FeCl_3$	H_2O	1	(*11*)	Arbutin becomes blue
c	Cholesterol	Alcohol	10	(*13*)	Precipitates additive compound of digitonin
d	Fehling's	Dil. K tartrate	3		Positive in 2 hours for picrotoxin, colocynthin, and scillitoxin
e	NH_4VO_3	H_2SO_4	0.5	(*9*)	Colors in few minutes
f	H_2SO_4	H_2O	92	(*2, 3*)	Colors in few minutes
g	$FeCl_3$	AcOH	Trace	(*8*)	Over H_2SO_4 containing trace of $FeCl_3$
h	HNO_3	H_2O	25	(*6*)	
i	Ac_2O		100	(*10, 12*)	Solution in Ac_2O over concd. H_2SO_4
j	H_3PO_4	H_2O	85	(*5*)	1 hour's standing
k	$ZnCl_2$	15 per cent HCl	3	(*1, 7*)	Immediate colors
l	Urotropin	H_2SO_4	0.05		Immediate colors

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Received June 16, 1934.

Peru Uses New Method of Extracting Quinine from Cinchona. Some publicity has recently been given by the Callao-Lima press to a more economic method of extracting quinine from the bark of the cinchona plant, which is found in abundance in the jungle regions of Peru. Experiments conducted by Señor Franciles Zamorra Silva in the laboratories of Señor Hersino V. Sanchez, at Monzon, Peru, have resulted in a new process of obtaining quinine alkaloids and salts which may greatly affect the local production and exportation of this drug.

The production of quinine salts and alkaloids from cinchona bark produced in Peru during the past few years is not equal to the local demand. The public health statistics indicate that an average of over 2000 cases in the charity hospitals of the city of Lima alone are annually treated with quinine, and epidemics of malaria necessitating its use occur frequently throughout the provincial districts of the Republic. Any method leading to the greater economic production of this drug receives the attention of the Peruvian Government.

Constant-Temperature High-Pressure Laboratory Autoclave

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A SMALL high-pressure autoclave, particularly suited for liquid-phase hydrogenation, was described by Peters and Stanger (*1*). The unit is heated electrically and well lagged on the outside. Stirring is obtained by rocking and the connection to the source of hydrogen is by means of a coil of flexible copper tubing. This design avoids the use of packing glands, since there are no moving parts inside the autoclave. Equipment of similar type, but smaller in size, is now available from supply houses as regular laboratory equipment.

While well suited for the preparation of many compounds by hydrogenation, autoclaves of this type are not particularly well adapted to a study of catalysts, especially active catalysts. Whenever the reaction is sufficiently exothermic and sufficiently fast, the amount of heat given off will raise the temperature considerably and accurate data cannot be readily obtained regarding the activity of the catalyst. Furthermore, in cases where either the compound being hydrogenated or the hydrogenation product is subject to thermal decomposition, and in cases where the reaction may take alternative courses at different temperatures, much better temperature control is desirable than can be achieved with this type of autoclave.

The autoclave described below retains all the advantages of the Peters and Stanger design, at the same time permitting accurate control of the temperature, practically independently of the heat evolved during the reaction. This is accomplished simply by surrounding the reaction tube with a jacket filled with a suitably chosen liquid, which is kept at its boiling point.

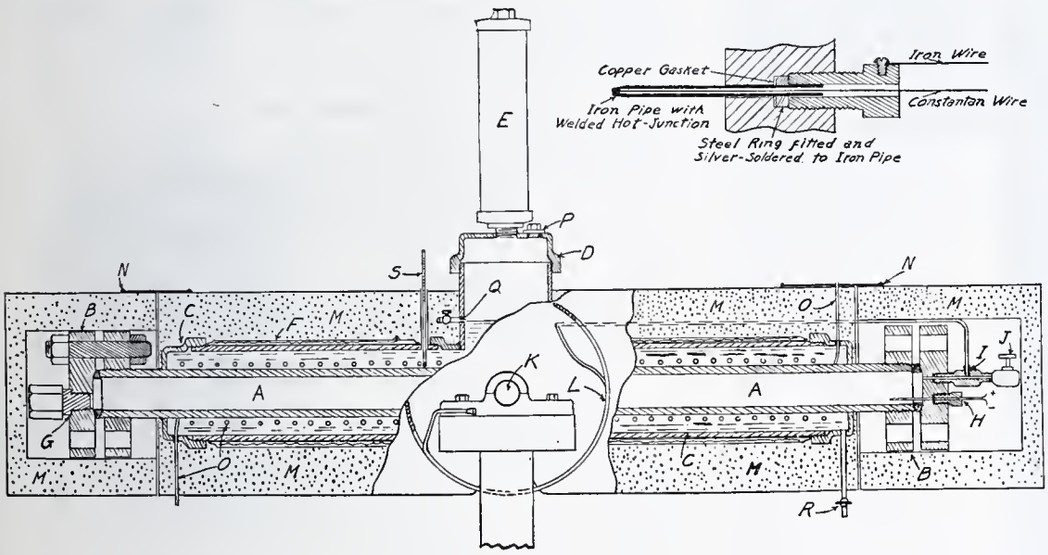

Figure 1. Constant-Temperature Autoclave

Description of Apparatus

The autoclave (Figure 1) is made of a 122-cm. length of seamless steel tubing 50 mm. in inside diameter and 75 mm. in outside diameter, *A*. This tube is closed at both ends by means of a steel flange, *B*, and a lens connection of the classical type. A jacket, *C*, made of standard 5-inch (12.5-cm.) pipe and fittings, is welded to this tube. The jacket is surmounted in the middle by a dome, *D*, which prevents splashing of the liquid up into the reflux condenser, *E*. The jacket is heated on the outside by means of strip heaters, *F*. Suitable connections are made in one flange for a liquid and catalyst inlet, *G*, and in the other for a hydrogen inlet, *I*, a blow-off valve, *J*, and a thermocouple, *H*. This latter is made of pure iron tubing containing an insulated constantan wire. No sheath is used, so that there is no lag in reading the temperature of the liquid. The fitting of the thermocouple through the flange is illustrated in the insert in Figure 1.

The autoclave is rocked 20 times per minute over a 30° arc. The axis, *K*, is horizontal and perpendicular to the longitudinal axis of the autoclave and at its middle. The hydrogen inlet coil, *L*, consists of 5 meters of hard-drawn copper tubing 6.5 mm. in outside diameter and 3.5 mm. in inside diameter wound into a coil about 30 cm. in diameter. The water connections to the reflux condenser are brought back near the axis of rotation and connected to the stationary pipes by means of rubber tubing. The entire autoclave is heavily lagged with magnesia lagging, *M*, including two large caps which are held over the ends of the tube by means of hooks, *N*. A 6-meter length of ordinary copper tubing, 5 mm. outside diameter, is coiled around the pressure tube within the jacket. The purpose of this coil, *O*, is to permit rapid cooling of the thermostatic liquid at the end of a run, since the heavy lagging would otherwise make it necessary to wait several hours before the charge was cooled down to room temperature. The thermostatic liquid is put in the jacket through a plug opening, *P*, leveled at cock *Q*, and drained off through cock *R*. Its temperature is taken with the thermometer, *S*.

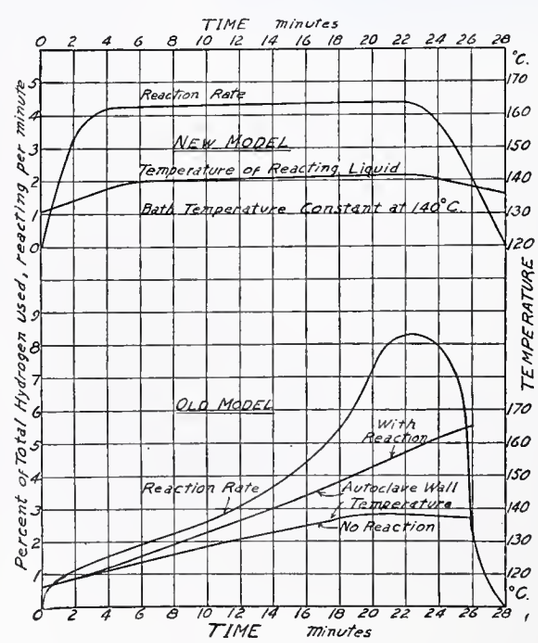

Figure 2. Comparison between New and Old Models of Autoclaves

This unit has been used at temperatures up to 280° C. and pressures up to 218 atmospheres. Most of the work was done at 150° C. and 68 atmospheres pressure using a mixture of ethylene glycol and water as the thermostatic liquid. Under those conditions 1 liter of furfural in the presence of 40 grams of copper chromite catalyst, regardless of activity, can be hydrogenated, maintaining the temperature of the reacting liquid constant within 2° C. at an equilibrium temperature just above the temperature of the thermostatic bath. The equilibrium temperature is maintained for approximately 70 per cent of the time for the run.

Figure 2 demonstrates the difference between the old and the modified models of the Peters and Stanger type of autoclave. Since no temperature equilibrium was obtained with the old type, comparison between various batches of catalyst was very difficult and of little value when applied to large-scale operation in a well controlled autoclave of a different type. The long equilibrium period obtained in the new model makes comparison between various catalysts easy and reliable.

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An Improved Fat-Extraction Apparatus

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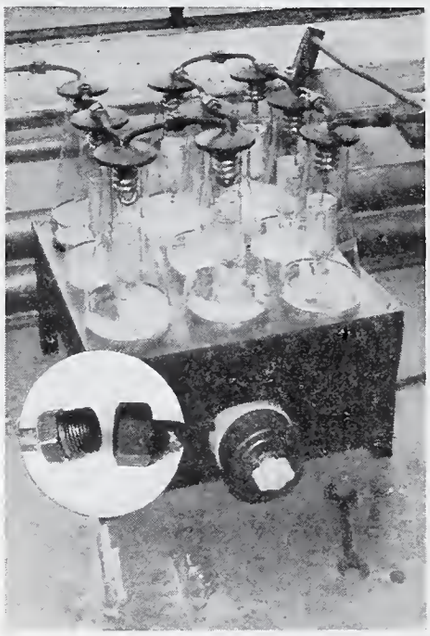

Figure 1. Assembly of Apparatus

While numerous types of apparatus for fat extraction have been developed, practically all have some features which are not entirely satisfactory. After numerous tests it was found that the equipment best suited for the purposes of this laboratory consisted of extraction flasks equipped with glass siphon cups and copper covers fitted with a coiled block-tin condenser. This apparatus has been described in detail, including an assembly drawing, by the Joint Rubber Insulation Committee (*1*). During the first months that this equipment was in use the block-tin condensers for the different flasks were connected by short pieces of rubber tubing. When new, the rubber tubing was difficult to apply without an occasional slip and knocking together of the flasks. After the tubing had been used for a time, it stretched and was not sufficiently tight to prevent leakage and a consequent loss of the vaporized solvent.

In order to obviate this continual inconvenience the condensers were connected with 0.125-inch ground-joint, brass unions, soldered to the ends of the block-tin condenser tubing. Figure 1 shows the fat-extraction apparatus with extraction flasks, condensers, and brass unions completely assembled. The insert shows the construction of the unions and the method of attaching them to the tubing, although it does not satisfactorily illustrate the ground joint.

The advantages of using the brass unions in place of the rubber tubing are: The brass unions can be opened or closed more rapidly than a connection can be made with rubber tubing. There is practically no wear on the unions and hence no need for replacement as in the case of rubber tubing. The joints will stand greater water pressure; therefore a greater volume of water can flow through the condenser, thus increasing the efficiency of the condensing surface. The ground joints make a close connection and there is no leakage of water. The brass unions are rigid and individual flasks have no tendency to tip.

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Preventing Bumping in Vacuum Distillations

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Prevention of bumping in vacuum distillation may be accomplished by using a flask with ground glass fused into the interior. The apparatus is easy to clean, may be used repeatedly, and is superior in some respects to other devices commonly used in the laboratory.

Pyrex glass is powdered in a mortar so that the largest sizes are not more than 1 to 1.5 mm. No attempt is made to separate the powder from the larger particles. Enough of the ground glass is put into a flask to cover thoroughly the lower half of its interior surface. The flask is then rotated in a flame and the desired portion heated high enough to soften the glass and cause the particles to become attached firmly. It is usually necessary to blow the flask a little to correct major deformations. After annealing, the flask is ready for use. Best results in distillation are secured when the coating of powdered glass is as thick as possible.

Distillation is carried out in the ordinary manner using an oil bath. In place of the usual bumping a little foaming occurs which fills the upper half of the flask. After this initial activity the surface subsides at once and remains relatively quiet during the remainder of the distillation. After use the flask is cleaned in the ordinary manner with acids or organic solvents and dried. Repeated use in this manner showed no diminution in its effectiveness in preventing bumping. Re-use without cleaning is possible, but prevention of bumping is not so effective.

These flasks are especially serviceable in the distillation of liquids which are sensitive to oxidation from the current of air which is frequently used. They are far superior to the common ebullator tubes.

Received June 20, 1934.

Rubber Stopper Remolding for Reduced Pressure Filtration

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THE many forms of Gooch-type filtering crucibles with their multiplicity of sizes, wall tapers, and heights introduce the problem of providing rubber adapters for inserting the crucible into holder for use in vacuum filtration (*1–3*). Fritted glass, quartz, or porous-bottomed porcelain crucibles as well as platinum Gooch Monroe crucibles are examples in question. The inverted perforated stoppers here described are substitutes for stock apparatus (*1–3*), but have the advantage that the dimensions obtainable are variable over a much wider range than is possible using special molded rubber forms.

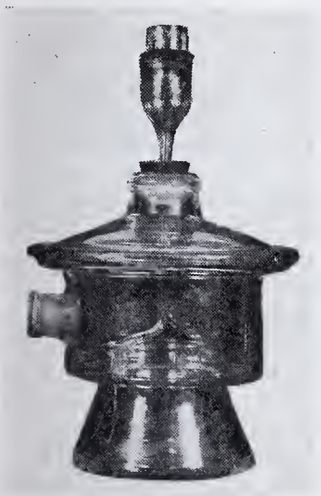

Figure 1. Filtering Assembly

8-inch (200-mm.) vacuum desiccator, 250-ml. beaker, and 25 × 37 mm. sintered glass crucible supported in a special filtering tube, using No. 7 stopper with 28-mm. hole.

Desirable rubber adapters for supporting crucibles in filter assemblies, such as those illustrated in Figures 1 and 2, provide a well-tapered outside diameter, a curving tapered inside surface to provide minimum contact with the filtering crucible, and gas-tight contacts at both surfaces. Following such a design, a given rubber adapter will fit the greatest number of funnel supports and crucibles having slight variations in dimensions. The use of a large rubber stopper with a small hole to fit Büchner funnel stems of comparatively small bore is difficult because the stopper often pulls through, with resultant breakage. This situation is impossible when using the modified stopper. The wide midsection flange prevents the troublesome cone deformation under pressure which causes the ordinary stopper form to pull through.

Table I. Dimensions of Stoppers, Cork Borer, and Inverted Finished Stoppers

Rubber Stopper No.	Stopper Diameter Top	Stopper Diameter Bottom	Cork Borer Diameter	Inverted-Stopper Measurements Top[a]	Middle[b]	Bottom[c]	Hole[d]
	Mm.	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*
13	70	60	43	57	75	63	42
13	70	60	35	60	76	59	34
12	64	58	35	53	70	53	34
11	56	50	35	45	60	53	35
10	50	42	35	44	52	45	34
10	50	42	28	42	55	43	25
9	45	37	28	35	47	39	27
9	45	37	25	35	47	40	23
8	40	32	25	35	44	37	23
8	40	32	28	32	43	36	27
7	37	30	25	31	40	33	23
7	37	30	28	32	40	32	33

[a] Diameter of circle made by sharp edge at top of stopper.
[b] Largest diameter at extreme midsection edge.
[c] Diameter of outside edge of bottom.
[d] Diameter at small end of curving tapered conical center hole.

The ordinary cork borer set does not extend to sizes sufficiently large to make the stoppers as shown in Figure 3. Cork borers of 1-, 1.25-, 1.5-, and 1.75-inch (2.5-, 3.1-, 3.7-, and 4.4-cm.) outside diameter are made from brass tubing having a 1-mm. wall thickness, sharpened at one end by making a tapering cut in the lathe on the outside, and tapered inside at the other end to provide a snug fit for the wooden hand support. The 1.75-inch (4.4-cm.) cork borer parts are shown in Figure 2. The wooden handle is turned in the lathe as shown, starting with a wooden roll paper end, which has a center hole already supplied for use in removing the rubber core cut from a stopper. A No. 13 rubber stopper is shown cut as desired in the top center object in Figure 3. The remaining forms are made from different sized stoppers and hole dimensions and are finally formed into shape by being turned inside out.

Figure 2. Remolded Rubber Stoppers

Left, small sintered-glass filtering crucible, 25 × 37 mm.; No. 7 stopper using 25-mm. cork borer; glass funnel, 37 mm. diameter at top; side-arm filtering test tube, 25 × 37 mm.; 250-ml. Soxhlet flask to support filter tube

Center, 43-mm. cork borer and wooden handle.

Right, large sintered-glass filtering crucible, 37 × 60 mm.; No. 13 stopper, using 35-mm. cork borer; glass funnel, 75-mm. diameter at top; 250-mm. filtering flask.

Large stoppers must have large holes. The minimum hole in a No. 13 stopper which will permit of its being turned inside out is 35 mm. [approximately 1.5-inch (3.1-cm.) cork borer]. To provide smaller holes in large stoppers, small stoppers after inversion are placed inside larger stoppers, as shown in

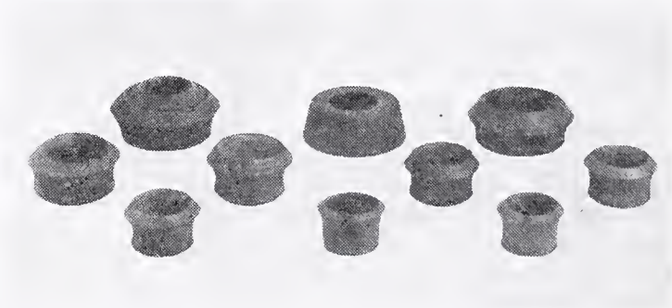

Figure 3. Finished Stoppers

Stoppers in Table I after inversion.

the upper left-hand object in Figure 3. The hole must be cut exactly in the center of the stopper. Failure to do this results in an inverted stopper having a flange of unequal width and an oval shape. A little 3-in-1 Oil is used to lubricate the cork borer. With large cork borers, cutting straight through the stopper is easier than with small borers. The cork borer can be withdrawn from a partially cut stopper for application of additional lubricant. The lower outside surface of the inverted stopper can be sandpapered to smooth out slight imperfections as a result of an imperfect cut. If the inverted stopper is too tall it is slipped over the cork borer and a razor blade is passed around and through the stopper to shorten it to the desired extent. The sanding of the lower outside edge is carried out with the stopper held as for shortening.

The apparatus and materials described and illustrated in this work are all standard laboratory equipment, with the exception of the large cork borers which should be made available as standard laboratory apparatus.

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(2) Spencer, *Ibid.*, 4, 614 (1912).
(3) Thomas Co., A. H., Catalog, 1931 ed., Items 4196, 4198, 4200, 4204, and 4206.

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A Differential Pressure Control Mechanism for Vacuum Distillation

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The advantages of pressure-regulating devices which require only intermittent operation of the pump over those requiring continuous pumping have only recently been appreciated. In a review of the literature on the subject by Hershberg and Huntress (*1*) only five of some thirty publications cited relate to the intermittent pumping type, and these, with but one exception, have all appeared within the past two years. To these may be added one more recent publication (*4*).

A decided advance in pressure-control technic was contributed by Hershberg and Huntress (*2*) in their publication describing a novel manostat in which sulfuric acid constitutes the manostatic liquid. The latter, with an appropriate thermionic relay and flutter valve, is claimed to permit pressure control within ±0.015 mm. of mercury. To use this device, however, they found it necessary to make the pump operation continuous and to use three valves to bleed in air at atmospheric pressure for the adjustment.

In a distillation system intended for precision work, which should be reasonably tight to begin with, any unavoidable minor leaks should require but very infrequent pumping for adjustment. The use of continuous pumping is therefore not only annoying, particularly where distillations over long periods are involved, but makes it very difficult to detect losses of the more highly volatile substances, a source of error generally not fully appreciated. With intermittent pumping such losses would ordinarily be detected early, as any increase in frequency of pumping over that occasionally necessary for compensation becomes at once an audible warning of leaks and inadequacies in the condensing system. It is thus particularly valuable as a safeguard against the loss of important volatile constituents.

The pressure-control scheme described in this paper takes advantage of the sensitive Hershberg-Huntress (*2*) sulfuric acid manostat, so adapted as to make possible accurate pressure control with the pump operating intermittently. Sulfuric acid is used as a manometric liquid, and a convenient simple U-type manometer of high sensitivity is included as a part of the system. A manometer of this kind, in view of its simplicity, and high sensitivity, should prove a generally useful device for laboratory purposes. As a rule, lighter liquids, such as dibutylphthalate and oils, cannot be used in U-type manometers, except in open-arm forms such as the Hickman mercury vapor pump gage, as it is virtually impossible to dislodge the liquid from the closed end even at very low pressures, owing probably to surface tension. For similar reasons inclined mercury manometers (*4*), although they provide magnified movement of the mercury thread, are not sufficiently rapid in response to gradual pressure change to be useful for accurate readings. McLeod gages require tedious calibration, provide very limited range, and do not permit of continuous observation.

The sulfuric acid manometer, while it does not possess quite the degree of accuracy of the Hickman gage, is relatively simple in construction. It provides a convenient and ready means, particularly with pressure-control devices, for setting and maintaining fixed pressures.

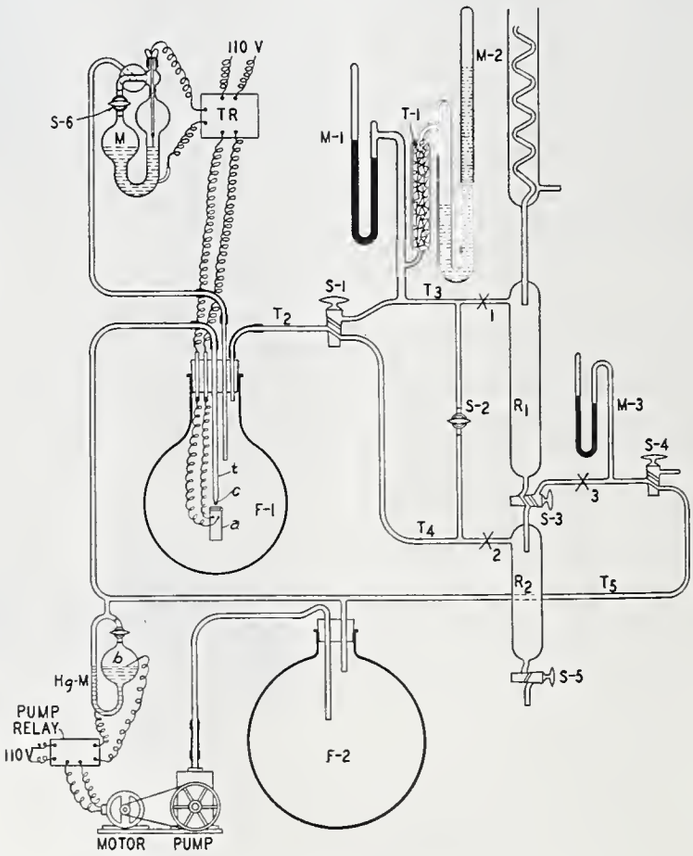

Figure 1. Diagram of Apparatus

Apparatus

Two distinct pressure systems are maintained with a pressure difference of from 4 to 30 mm. These are in intermittent communication with one another by way of a valve operated by a magnet, controlled in turn by a Hershberg-Huntress (*2*) sulfuric acid manostat and thermionic relay. In the low-pressure system, pressure is maintained only approximately constant by means of a mercury manostat relay, and may be from 4 to 30 mm. lower than the pressure in the distillation system. The flask containing the valve which is in direct communication with the distillation apparatus represents the other system, in which the pressure is accurately controlled.

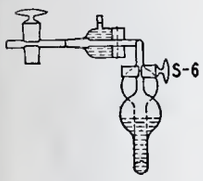

Figure 2

The valve-operating mechanism enclosed in flask *F*-1 consists of a small simple magnet (old type of telephone bell-ringing magnet), the movable part (hinged lid) of which is covered with a strip of smooth rubber. The magnet and a long 0.125-inch (0.32-cm.) tube, *t*, the end of which has a capillary opening, *c*, are securely fastened to a base as indicated. The movable part of the magnet effects intermittent closure of the capillary.

The sulfuric acid manostat and thermionic relay, *M* and *TR*, are essentially as described by Hershberg and Huntress (*2*), a mercury-sealed ground-glass joint (Figure 2) being substituted for the ground-steel joint used in their apparatus.

The mercury manostat (*Hg-M*) is similar to the sulfuric acid manostat in construction and provides for a wide range of pressures. It is rendered less sensitive than the ordinary U-type mercury manostat by making bulb *b* relatively large.

The manometer, *M*-2, is a simple U-type made from Pyrex glass tubing at least 2 cm. in inside diameter, to compensate for the high viscosity of the acid (*2*). Sulfuric acid, of the concentration used in the sulfuric acid manostat (sp. gr. 1.71), may be used as a manometer liquid, the apparatus being properly trapped to prevent diffusion of gases or vapors to or from the acid. Melville (*3*) mentions the use of sulfuric acid for such a purpose. After filling, it was carefully boiled out by gentle heating, the pressure having been reduced to 1 to 2 mm. of mercury; 7.9 mm. difference in acid level corresponded to 1 mm. pressure of mercury.

Flasks *F*-1 and *F*-2 are used to eliminate possible pressure fluctuations when the valve opens. It was noticed that with a pressure difference of 5 to 6 mm. in the two systems and with flask *F*-1 of 2-liter capacity, there was a movement of about 1 mm. in the sulfuric acid levels on opening and closing the valve. Substituting a 5-liter flask eliminated this difficulty entirely, with a pressure difference of 32 mm. of mercury in the two systems. Flask *F*-2 may be of any convenient size; 2-, 5-, and 12-liter flasks and a 20-gallon (75.7-liter) tank gave equally good results, the only difference being somewhat more frequent starting and stopping of the vacuum pump with the smaller vessels.

T_1 is a trap filled with quicklime. Other traps may be used at T_2, T_3, etc.

The entire apparatus with the exception of the pump was made portable as in the case of the Hershberg-Huntress scheme (*1*), by mounting it on an instrument board with a fixed base, connections with distillation apparatus being made with rubber tubing at X_1, X_2, and X_3.

The general principle of dual pressure control described above can be applied to some advantage even with the pump (mechanical or water-aspirator type) continuously operated. When so used the mercury manostat, *Hg-M*, and pump relay are eliminated.

Leakage or an inadequate condensing system would manifest itself by too frequent operation of the thermionic relay, *TR*, and valve.

Operation

For use with a fractionating column the following sequence has been found desirable and permits the taking of fractions during the distillation without disturbing the pressure:

To evacuate the system the manostat stopcock, *S*-6, is opened and stopcocks *S*-1, *S*-3, and *S*-4 are turned so as to connect *F*-1 with *F*-2, and the by-pass between receivers R_1 and R_2 is opened through *S*-2, so that the entire system is now connected directly with *F*-2 and the vacuum pump. When the required pressure is reached, *S*-2 is closed and *S*-3 is turned so as to connect R_1 and R_2. At the same time the sulfuric acid manostat is adjusted so that capillary tip *c* of tube *t* inside *F*-1 is closed by the rubber pad as discussed above and the manostat stopcock is closed. *S*-1 is turned so as to connect *F*-1 with R_1. Evacuation of *F*-2 is continued until the desired pressure difference between the two systems is reached, as observed on manometers *M*-1 and *M*-3, when the mercury manostat, *Hg-M*, is adjusted.

To remove a fraction of the distillate from the receiver R_2, the following procedure is recommended:

S-3 is turned to shut off R_1 from R_2, and *S*-4 is opened to the atmosphere. Through *S*-3, R_2 is brought to atmospheric pressure, and the fraction is run out through *S*-5. During this operation, the pressure in the distillation apparatus as a whole is being maintained constant. After the fraction has been taken, the pressure in R_2 is reduced to that which prevails in the still, in two stages as follows: R_2 is connected with *F*-2 through *S*-4, and evacuation continued until the pressure recorded on *M*-3 has practically reached that of *M*, and *S*-4 is promptly turned off. Final adjustment of the pressure in R_2 is accomplished by establishing communication between it and *F*-1 through *S*-1, after which all stopcocks are turned to their original positions.

Summary

In the pressure-control assembly here described, a dual pressure system is maintained with the two systems about 4 to 30 mm. apart. One vessel, in continuous communication with the distillation system, constitutes the higher pressure system, the pressure being maintained constant by means of a valve operated by a magnet controlled by a Hershberg-Huntress sulfuric acid manostat and thermionic relay. Another vessel, in continuous communication with the pump but in intermittent communication with the first vessel, constitutes the lower pressure system, the pressure being maintained only approximately constant.

The pump operates only occasionally and is controlled in turn by a mercury manostat and relay.

The sulfuric acid U-type manometer described is about eight times as sensitive as the ordinary mercury manometer.

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(1) Hershberg and Huntress, Ind. Eng. Chem., Anal. Ed., **5**, 144 (1933).
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(4) Palkin, S., Ind. Eng. Chem., **25**, 95 (1933).

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A Simple Absorption Pipet

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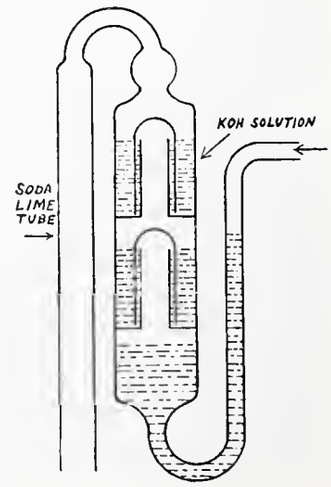
The accompanying diagram illustrates a carbon dioxide absorption tube for organic combustion analysis. Besides being simple in construction, it has the added advantages of being in one compact unit, easy to fill, easily hung on the balance, and much more rugged than the Liebig or Geissler bulbs. Very satisfactory results have been obtained from the use of this pipet.



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Agitator for Lamp-Method Sulfur Titrations

Lyle Dolan

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In the usual procedure for the determination of sulfur in petroleum products by the lamp method (A. S. T. M., D90–30T), it is specified that the carbonate solution in the absorption bulb be agitated during titration by alternately blowing and sucking by mouth on the exit side of the bulb. Considerable pressure is required to force the liquid backward and forward through the packing and, when running a large number of such analyses during a day, this operation becomes rather fatiguing and inefficient, particularly when, as is often the case, the connecting tube becomes partly obstructed by the packing.

This tedious and rather unsanitary procedure is obviated by the use of a simple arrangement, shown in the figure, which has been in continual and successful use in this laboratory for about 14 months. By simple manipulation of the conveniently located three-way stopcock a continuous and uniform agitation may be secured during titration and, when near the end point, the carbonate solution may be transferred rapidly backward and forward between the two bulbs.

The orifice shown in the line to the bulb is of the correct size to prevent any reagent being blown from the bulb when the three-way cock is wide open. Where the air pressure supply is high compared to the vacuum obtainable, more uniform operation can be secured by plugging the openings in the three-way cock and drilling suitably small holes to the air and vacuum sides of the cock.

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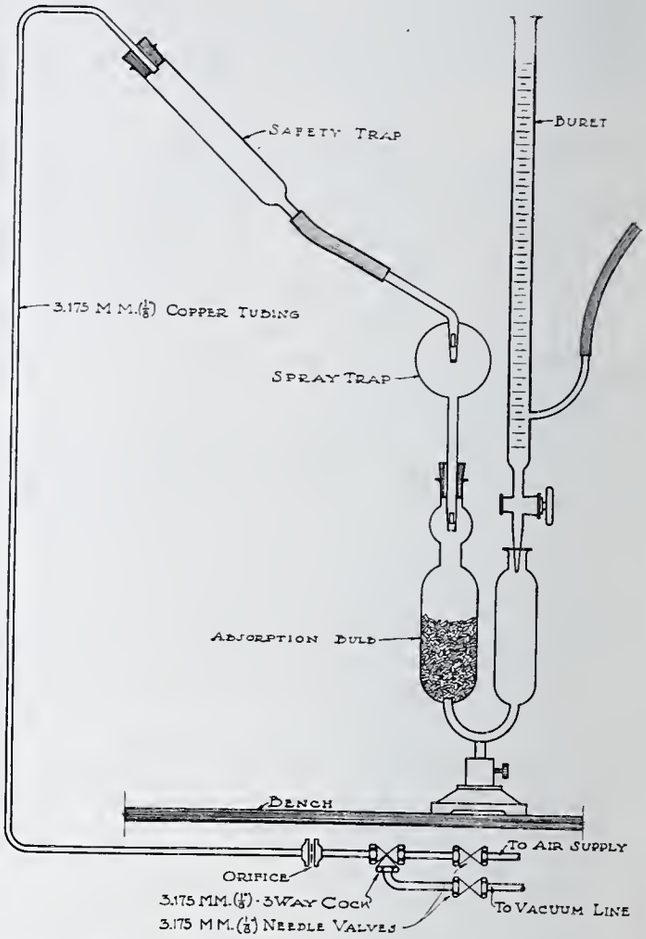

A Divided Titration Flask

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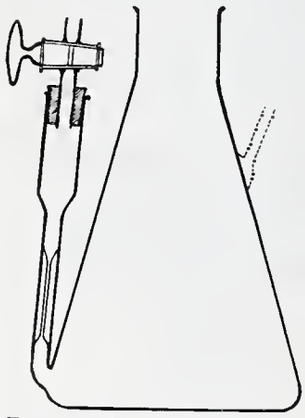

Divided Titration Flask

The simple and convenient divided-titration stirring rod recently described by Richardson (*3*) has been used by the writer for some time. Richardson has pointed out the advantages of speed, accuracy, and convenience offered in titrations. In many cases, particularly in the Kjeldahl nitrogen determination, titration is preferably made in a flask and the stirring rod is inconvenient. The flask here described is a simple device for extending the method and with slight modification is also suitable for differential electrometric titration.

The flask is easily made by sealing a capillary tube between two pieces of glass tubing, and attaching to an Erlenmeyer flask and test tube, as shown in the figure. The apparatus is preferably made of Pyrex, the capillary being about 3 cm. of 0.5-mm. tubing, and the test tube being of about 15 ml. capacity and diameter less than 1 cm. The rubber stopper with stopcock is preferable to a sealed-in stopcock, making the apparatus easier to clean.

In operation, the solution to be titrated is placed in the flask and a portion drawn into the side tube. Titration is made rapidly until the end point is passed, and part of the solution in the side tube run in. A more careful titration to the end point, with a final rinse of the side tube, completes the titration. With a buret having a time of over 1 minute, it is almost impossible to pass the end point, the liquid in the side tube always serving as a reserve and obviating annoying back-titration. With normal swirling for mixing during titration, there is very little disturbance of the liquid in the side tube and it will not splash onto the stopper.

The flask can be modified to make a very satisfactory arrangement for differential electrometric titration as described by Cox (*1*) and modified by MacInnes and Jones (*2*). A two-holed rubber stopper, carrying stopcock and a glass tube with platinum foil electrode, replaces the stopper and stopcock on the side tube. The second electrode may be placed in the solution through the mouth of the flask but is preferably inserted through a side tube, as shown by dotted lines. This second electrode has a rather narrow strip of foil and is easily attached by slip-on rubber tubing. Mechanical agitation is unnecessary in this titration, swirling by the hand being sufficient for thorough mixing.

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(1) Cox, *J. Am. Chem. Soc.*, 47, 2138 (1925).
(2) MacInnes and Jones, *Ibid.*, 48, 2831 (1926).
(3) Richardson, *Ibid.*, 55, 2794 (1933).

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HARRISON E. HOWE, EDITOR

A Method for Evaluating the Viscosity-Temperature Characteristics of Oils

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WITH the development of new refining processes by means of which the viscosity-temperature characteristics of oils may be varied appreciably, the problem of evaluating the viscosity characteristics of different lubricants over a wide range in temperature becomes increasingly important. This is especially true of automotive lubricants, because the mechanical parts must be lubricated satisfactorily both at relatively low temperatures and at the relatively high temperatures encountered in severe operating conditions.

A satisfactory motor lubricant must serve at least two purposes: (1) the lubricant must be sufficiently fluid at low temperatures so that the car can be started readily and the various parts may receive oil during starting; (2) the lubricant must be sufficiently viscous at higher temperatures so that the parts of the motor may not suffer undue wear during long periods of operation at engine temperatures. For these reasons, it is generally recognized that a lubricant whose viscosity changes slowly with temperature is more satisfactory under severe operating conditions than another lubricant whose viscosity changes rapidly with temperature.

The fact that an oil must be relatively viscous at higher temperatures is readily apparent since many of the parts to be lubricated operate at elevated temperatures. It may not be so obvious that an oil must be relatively fluid at low temperatures. Larson (*9*), Becker (*1*), and Blackwood and Rickles (*3*) have shown that the power required to start a car in cold weather is directly related to the viscosity of the crankcase lubricant at the starting temperatures. Lederer and Zublin (*11*) have shown that the pumpability of an oil at low temperatures is dependent in a large measure on the viscosity of the oil at operating temperatures and to a lesser degree on the pour point of the oil. For these reasons, it is desirable that the rate of change of viscosity with temperature for the crankcase lubricant be as low as possible.

Various means for evaluating and comparing oils with respect to their relative rates of change of viscosity with temperature are available. These may be listed as follows:

1. Ratio of the 100° F. (37.8° C.) viscosity to the 210° F. (98.9° C.) viscosity.
2. Viscosity index as developed by Dean and Davis (*7*) and later revised by Davis, Lapeyrouse, and Dean (*6*).
3. Viscosity slope number developed by Bell and Sharp (*2*) by means of arbitrary arithmetical scales superimposed on the A. S. T. M. viscosity-temperature chart, D-341-32-T.
4. Viscosity gradient devised by Clayden (*4*) for expressing the viscosity temperature slope of oils by means of angles and fundamental viscosity units.
5. Viscosity-gravity constant introduced by Hill and Coates (*8*) in 1928 as a means for evaluating the paraffinicity or naphthenicity of oils.
6. Viscosity gravity zones recommended by Larson and Schwaderer (*10*) in 1932 and 1933 as a means for graphical estimation of relative viscosity-temperature characteristics.
7. Gravity index (*12*) based on an empirical relation between viscosity-gravity constant and viscosity index.

Each of these several methods for comparing lubricating oils with respect to their viscosity-temperature characteristics may be divided roughly into two classes, depending upon whether they are based directly upon viscosity-temperature charts or upon a comparison with certain specific types of oil. Each method of classifying oils appears to have certain fairly well defined advantages and disadvantages, but there is no apparent means by which the advantages of each classification may be retained. None of the methods result in a quantitative expression of the actual viscosity at low or high temperatures. Therefore, for the purpose of obtaining further means of comparing oils in this respect it has appeared desirable to start with an entirely different reference basis. The purpose of this paper is to outline a method by means of which the viscosities of different oils may be compared quantitatively, either at the low temperatures encountered in winter starting or at the high temperatures encountered during motor operation.

With the present lack of information on the materials which compose petroleum, it appears practically impossible to develop a method for evaluating this characteristic of lubricating oils on an absolute basis. For this reason, practically any method devised at the present time for this purpose must be established on a relative and comparative basis. From the point of view of comparing the performance of lubricants in service in so far as this is dependent upon viscosity, it seems logical to evaluate oils at two temperature extremes, one high and one low. Also, practical engineering usefulness dictates that fundamental units such as the stoke or poise be used instead of arbitrary units of viscosity such as Saybolt seconds.

Table I. Viscosity-Temperature Relations of Oils

Zero Viscosity Factor	Kinematic Viscosity (Centistokes) 0° F.[a] (−17.8° C.)	100° F.[b] (37.8° C.)	210° F.[c] (98.9° C.)	400° F.[d] (204.4° C.)	Viscosity Index	Kinematic Viscosity (Centistokes) 0° F.[a] (−17.8° C.)	100° F.[b] (37.8° C.)	210° F.[c] (98.9° C.)	400° F.[d] (204.4° C.)	Viscosity Index	Kinematic Viscosity (Centistokes) 0° F.[a] (−17.8° C.)	100° F.[b] (37.8° C.)	210° F.[c] (98.9° C.)	400° F.[d] (204.4° C.)	Viscosity Index
0.1	143.1	17.12	5.0	1.62	187	329.2	28.29	7.0	2.01	170	787.1	48.12	10.0	2.52	155
0.2	286.2	21.70	5.0	1.53	158	658.4	34.23	7.0	1.80	153	1,574	58.14	10.0	2.28	141
0.4	572.4	24.80	5.0	1.32	139	1,317	40.92	7.0	1.65	133	3,148	69.35	10.0	2.09	126
0.6	858.6	27.45	5.0	1.25	122	1,975	45.34	7.0	1.57	119	4,723	77.31	10.0	1.99	115
0.8	1,145	29.40	5.0	1.21	109	2,634	48.50	7.0	1.52	110	6,297	82.78	10.0	1.93	108
1.0	1,431	30.90	5.0	1.19	99	3,292	51.21	7.0	1.49	101	7,871	87.50	10.0	1.88	101
2.0	2,862	36.10	5.0	1.11	65	6,584	60.02	7.0	1.39	74	15,742	102.7	10.0	1.75	81
4.0	5,724	42.04	5.0	1.04	25	13,170	69.94	7.0	1.30	44	31,484	121.0	10.0	1.65	56
6.0	8,586	45.89	5.0	1.01	−1	19,750	76.51	7.0	1.26	24	47,226	132.0	10.0	1.60	41
8.0	11,450	48.44	5.0	0.99	−18	26,340	80.95	7.0	1.23	10	62,968	141.1	10.0	1.55	28
10.0	14,310	50.87	5.0	0.97	−34	32,920	86.12	7.0	1.21	−6	78,710	148.2	10.0	1.53	18
20.0	28,620	58.13	5.0	0.92	−84	65,840	99.50	7.0	1.15	−47	157,420	169.5	10.0	1.46	−11
40.0	57,240	68.71	5.0	0.89	−155	131,700	112.0	7.0	1.10	−86	314,840	195.8	10.0	1.37	−48
60.0	85,860	71.18	5.0	0.86	−172	197,500	120.6	7.0	1.08	−113	472,260	210.4	10.0	1.35	−68
80.0	114,380	75.19	5.0	0.85	−198	263,400	127.6	7.0	1.06	−135	629,680	224.5	10.0	1.33	−87
100.0	143,100	78.20	5.0	0.84	−219	329,200	132.6	7.0	1.05	−151	787,100	233.7	10.0	1.31	−100
0.1	2,080	87.78	15.0	3.27	146	4,109	134.9	20.0	3.93	138	10,590	246.1	30.0	5.08	131
0.2	4,160	106.3	15.0	2.96	135	8,217	163.1	20.0	3.56	128	21,180	297.9	30.0	4.61	123
0.4	8,320	127.6	15.0	2.71	122	16,434	196.1	20.0	3.26	117	42,360	358.6	30.0	4.22	114
0.6	12,481	142.2	15.0	2.59	113	24,652	218.5	20.0	3.12	110	63,540	400.1	30.0	4.03	108
0.8	16,641	152.0	15.0	2.51	107	32,869	234.1	20.0	3.02	105	84,720	429.5	30.0	3.90	104
1.0	20,801	160.9	15.0	2.45	101	41,086	247.8	20.0	2.95	100	105,900	455.6	30.0	3.85	100
2.0	41,602	189.4	15.0	2.31	84	82,172	292.9	20.0	2.75	85	211,800	540.1	30.0	3.55	88
4.0	83,204	222.5	15.0	2.15	73	164,340	344.8	20.0	2.58	68	423,600	638.4	30.0	3.33	74
6.0	124,806	244.0	15.0	2.07	51	246,520	380.3	20.0	2.49	56	635,400	705.0	30.0	3.21	64
8.0	166,408	261.1	15.0	2.03	41	328,690	404.3	20.0	2.43	48	847,200	752.7	30.0	3.13	57
10.0	208,010	273.6	15.0	1.99	33	410,860	426.8	20.0	2.39	41	1,059,000	793.9	30.0	3.08	51
20.0	416,020	318.2	15.0	1.89	5	821,720	495.9	20.0	2.27	17	2,118,000	926.7	30.0	2.91	32
40.0	832,040	368.0	15.0	1.80	−26	1,643,440	575.0	20.0	2.16	−9	4,236,000	1080	30.0	2.77	9
60.0	1,248,060	400.2	15.0	1.75	−45	2,465,160	626.1	20.0	2.09	−26	6,354,000	1176	30.0	2.69	−6
80.0	1,664,080	423.6	15.0	1.72	−59	3,286,880	665.7	20.0	2.05	−40	8,472,000	1250	30.0	2.64	−17
100.0	2,080,100	443.0	15.0	1.70	−71	4,108,600	697.4	20.0	2.03	−50	10,590,000	1311	30.0	2.59	−29
0.1	20,701	377.4	40.0	6.08	127										
0.2	41,402	457.0	40.0	5.11	120										
0.4	82,804	548.9	40.0	5.07	113										
0.6	124,206	615.8	40.0	4.83	107										
0.8	165,608	661.1	40.0	4.67	104										
1.0	207,010	702.0	40.0	4.56	100										
2.0	414,020	833.8	40.0	4.25	90										
4.0	828,040	987.8	40.0	3.97	77										
6.0	1,242,060	1093	40.0	3.84	69										
8.0	1,656,080	1166	40.0	3.74	63										
10.0	2,070,100	1233	40.0	3.67	57										
20.0	4,140,200	1438	40.0	3.47	40										
40.0	8,280,400	1686	40.0	3.29	19										
60.0	12,420,600	1844	40.0	3.20	6										
80.0	16,560,800	1963	40.0	3.14	−4										
100.0	20,701,000	2058	40.0	3.08	−12										

[a] For oils having a zero viscosity factor of 1, the viscosity at 0° F. (−17.8° C.) was calculated from the 100° F. (37.8° C.) and 210° F. (98.9° C.) viscosities by Equation 2. All other viscosities at 0° F. are definite percentage amounts, depending upon the numerical value of the zero viscosity factor of the 0° F. viscosity of the reference oil.

[b] For oils which have a zero viscosity factor of 1, the 100° F. viscosity was calculated from the 210° F. viscosity by Equation 1. All other viscosities at 100° F. were calculated by means of Equation 2, since the viscosities of these various oils were known at temperatures of 210° and 0° F.

[c] Viscosity at 210° F., at which temperature all oils which are to be rated in terms of viscosity ratio at 0° F. have equal viscosity.

[d] Viscosity calculated by Equation 2.

Proposed Method

The proposed method for comparing the viscosity-temperature characteristics of lubricating oils is largely mathemetical in nature and depends on relatively simple procedures and concepts. The steps may be outlined as follows:

1. A single type of oil is used for reference purposes.
2. Comparisons are made with oils having equal viscosities at 210° F. (98.9° C.).
3. The 100° F. (37.8° C.) viscosity of the reference oil is expressed in terms of its 210° F. (98.9° C.) viscosity by a simple equation.
4. The viscosity of the reference oil can be calculated at any other temperature by known relations.
5. All oils, if matched as to viscosity at 210° F. (98.9° C.), have a definite viscosity ratio at 0° F. (−17.8° C.) with respect to the reference oil.
6. The 100° F. (37.8° C.) viscosity of any oil having known viscosities at 0° F. (−17.8° C.) and 210° F. (98.9° C.) can be calculated.
7. The mathematical results can be expressed accurately by means of a simple nomograph.

The 100° F. (37.8° C.) viscosities, Y, of the reference oils were calculated for given viscosities at 210° F. (98.9° C.), X, by means of the following equation.

$$\log_{10} Y = 1.502 \log_{10} X + 0.4400 \qquad (1)$$

This equation may be considered as defining the viscosity characteristics of hypothetical oils for the purpose of establishing a reference standard, or it may be considered as defining the viscosity characteristics of actual oils, since for all practical purposes the equation satisfactorily correlates the viscosity-temperature characteristics of oils refined from an extreme type of paraffin-base crude oil.

When the viscosities of a lubricating oil are known at two temperatures, the viscosity at a third temperature can be calculated by well-known relations. Two equations which are probably better known than others are Cragoe's (*5*) and the one employed by the American Society for Testing Materials for developing the viscosity-temperature chart designated as D-341-32-T. These two equations result in approximately similar results, but the calculations in this paper are based on the A. S. T. M. equation, which is probably more widely known and used than Cragoe's equation. The A. S. T. M. equation (*13*) is:

$$\log \log (KV + 0.8) = A \log T + B \qquad (2)$$

where KV is kinematic viscosity in centistokes, T is absolute temperature, and A and B are constants. Use of this equation instead of the A.S.T.M. viscosity-temperature chart is desirable, because the errors inherent in graphical extrapolation and interpolation are eliminated.

The results presented in this paper are based on Equations 1 and 2, plus the concept that oils matched as to viscosity at 210° F. (98.9° C.) have different viscosities at 0° F. (−17.8° C.) depending upon their viscosity-temperature characteristics, and that the latter may be expressed as the ratio of the 0° F. (−17.8° C.) viscosity of any given oil and the 0° F. (−17.8° C.) viscosity of a reference oil. For conciseness, this viscosity ratio at 0° F. (−17.8° C.) has been termed the "zero viscosity factor." The numerical value of this factor is a quantitative measure of the 0° F. (−17.8° C.) viscosity of an oil, since the product of the 0° F. (−17.8° C.) viscosity of the reference oil and the determined zero viscosity factor is the 0° F. (−17.8° C.) viscosity of that oil. All viscosities are expressed in terms of kinematic viscosity (centistokes), in order that fundamental units may be used.

By choosing any given viscosity at 210° F. (98.9° C.) for the reference oil, and by assigning a definite value for the viscosity ratio at 0° F. (−17.8° C.), it is possible to calculate the 0° F. (−17.8° C.) and 100° F. (37.8° C.) viscosities of oils having the assumed viscosity characteristics.

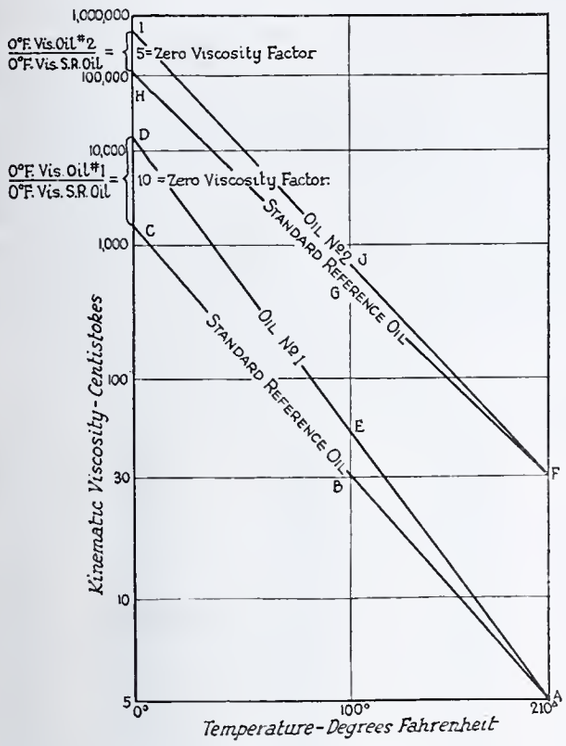

Figure 1. Graphical Representation of Method Used in Developing Zero Viscosity Factor

The method followed in establishing the zero viscosity factor mathematically is indicated graphically by Figure 1.

The viscosity-temperature characteristics of four oils are represented, two oils having 210° F. (98.9° C.) viscosities of 5 centistokes and the remaining two oils having 210° F. (98.9° C.) viscosities of 30 centistokes. The 100° F. (37.8° C.) viscosities of the light and heavy reference oils designated by points *B* and *G*, respectively, were obtained from the 210° F. (98.9° C.) viscosities of 5 and 30 centistokes, respectively, by means of Equation 1. The 0° F. (−17.8° C.) viscosity of the light and heavy reference oils were obtained from their respective viscosities at 100° F. (37.8° C.) and 210° F. (98.9° C.) by solving Equation 2. The 0° F. (−17.8° C.) viscosity of oil 1 was obtained by multiplying the 0° F. (−17.8° C.) viscosity of the light reference oil by a zero viscosity factor of 10 and its 100° F. (37.8° C.) viscosity was obtained by substituting viscosities at 0° F. (−17.8° C.) and 210° F. (98.9° C.) in Equation 2.

Oil 2 is matched as to viscosity at 210° F. (98.9° C.) with a reference oil having a viscosity at 210° F. (98.9° C.) of 30 centistokes. By assuming a zero viscosity factor of 5 for oil 2, it is possible to calculate the viscosities of oil 2 at temperatures of 100° F. (37.8° C.) and 0° F. (−17.8° C.). Having established the 100° F. (37.8° C.) and 210° F. (98.9° C.) viscosities of oils in this manner, it is possible to calculate the viscosity index of oils having definite zero viscosity factors. Also the viscosity of oils having definite viscosity relations at 0° F. (−17.8° C.) may be calculated at any desired temperature (say, 400° F.) by solving Equation 2.

The viscosity-temperature characteristics of a large number of oils having different 210° F. (98.9° C.) viscosities and different zero viscosity factors have been calculated by the method indicated above. Calculated data for oils having viscosities at 210° F. (98.9° C.) from 5.0 centistokes (a light oil) to 40.0 centistokes (an extremely heavy oil) and having zero viscosity factors from 0.1 to 100 are contained in Table I.

The data contained in Table I have been used as a basis for constructing a nomograph (Figure 2) by means of which the zero viscosity factor of oils may be determined readily from the viscosity at 210° F. (98.9° C.) and 100° F. (37.8° C.). The chart is used by connecting the points representing the viscosities of an oil at 210° F. (98.9° C.) and 100° F. (37.8° C.) with a straight edge and reading off the value of the zero viscosity factor at the point where the straight edge intersects the sloping line on the right-hand side of the chart. The three scales shown are logarithmic and interpolations should be made with this in mind.

The data contained in Table I indicate further that the viscosity index of oils is not an absolute criterion of relative viscosities at low temperatures. For example, oils which are 10 times more viscous than the standard reference oils at 0° F. (−17.8° C.) and have 210° F. (98.9° C.) viscosities of 5.0, 15, and 30 centistokes require viscosity indexes of −34, +30, and +51, respectively. These variations in viscosity index are probably greater than would be anticipated for oils having a constant viscosity ratio at 0° F. (−17.8° C.). It is indicated therefore that viscosity index alone is not sufficient for accurately evaluating the 0° F. (−17.8° C.) viscosity characteristics of oils. Oils having a zero viscosity factor of 1.0 have viscosity index values of approximately 100 through a range in viscosity at 210° F. (98.9° C.) of 5.0 to 40 centistokes. The relation between viscosity index, 210° F. (98.9° C.) viscosity, and zero viscosity factor of oils is reversed when oils have zero viscosity factors less than 1.0. For example, oils having a zero viscosity factor of 0.1 and 210° F. (98.9° C.) viscosities of 5.0, 15, and 30 centistokes have viscosity indexes of 187, 143, and 131, respectively. Significant differences in viscosity index are therefore less important in the case of light oils than in the case of relatively heavy oils.

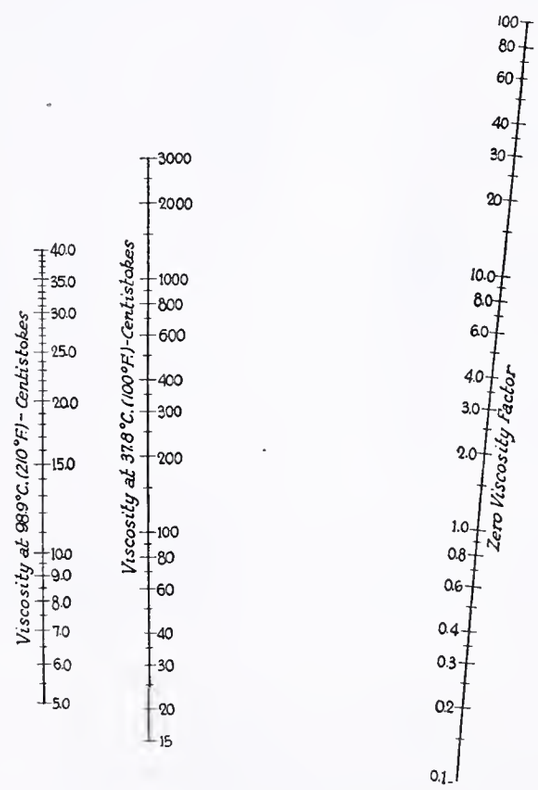

Figure 2. Nomograph for Obtaining Zero Viscosity Factor of Oils

Variations in viscosity index such as those indicated above are not unusual when the viscosity index concept is applied to theoretical considerations. If the ideal lubricant is defined as an oil whose viscosity does not change with temperature, it is possible to calculate the maximum theoretical viscosity index for such oils having different viscosities at 210° F. (98.9° C.). When these calculations are made, it is found

that the viscosity indexes would be approximately 250 for a light oil, and 200 and 160 for medium and heavy oils, respectively. In other words, the maximum theoretical viscosity index of hypothetical lubricants decreases rapidly with increasing viscosity at 210° F. (98.9° C.). This effect is indicated in Figure 3 for oils having extremely low zero viscosity factors.

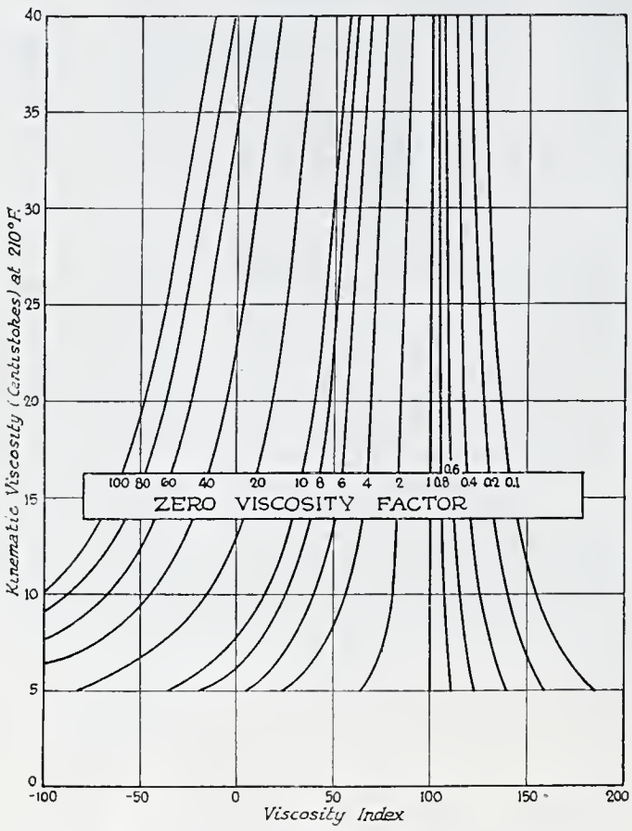

FIGURE 3. RELATION BETWEEN VISCOSITY INDEX AND ZERO VISCOSITY FACTOR

It is evident that the zero viscosity factor offers a ready means for approximating closely the 0° F. (−17.8° C.) viscosities of oils without resorting to an A. S. T. M. viscosity-temperature chart, provided a ready means for obtaining the 0° F. (−17.8° C.) viscosity of the reference oils is available. Fortunately, relatively simple means exist by which the 0° F. (−17.8° C.) viscosity of reference oils may be calculated. This equation is

$$\log_{10} Z = 2.383 \log_{10} X + 1.5046 \qquad (3)$$

where Z is the viscosity in centistokes at 0° F. (−17.8° C.) and X is the viscosity in centistokes at 210° F. (98.9° C.). Also, the 0° F. (−17.8° C.) viscosity of reference oils can be calculated from the 100° F. (37.8° C.) viscosity by the equation

$$\log_{10} Z = 1.586 \log_{10} Y + 0.8065 \qquad (4)$$

where Z and Y are the viscosities in centistokes at 0° F. (−17.8° C.) and 100° F. (37.8° C.), respectively.

Table II contains data relating to the 0° F. (−17.8° C.) viscosity of reference oils for viscosities varying from 5.0 to 40 centistokes at 210° F. (98.9° C.). The data in column A were obtained by applying successively Equations 1 and 2, while the data in columns B and C were obtained from Equations 3 and 4, respectively. The results in columns B and C do not vary by more than approximately 3 per cent from the results in column A. It follows therefore that the viscosity of an oil at 0° F. (−17.8° C.) may be approximated readily by use of the nomograph contained in Figure 2 and the viscosity data on reference oils contained in Table II or by use of the nomograph and Equations 3 or 4.

The viscosity of oils at a temperature of 400° F. (204.4° C.) can be estimated fairly closely by the use of the zero viscosity factor and the data contained in Table I. For example, if an oil were found to have a zero viscosity factor of 5 and were known to have a 210° F. (98.9° C.) viscosity of 15.0 centistokes, the data contained in Table I indicate that this oil would have a viscosity at 400° F. (204.4° C.) of approximately 2.1 centistokes. It is also possible to obtain the 400° F. (204.4 C.) viscosity of oils having 210° F. (98.9° C.) viscosities other than those listed in Table I by interpolation between the tabulated values. It is further possible that a nomograph based on the zero viscosity factor, viscosity at 210° F. (98.9° C.), and viscosity at 400° F. (204.4° C.) might be developed.

TABLE II. VISCOSITY-TEMPERATURE RELATIONS OF REFERENCE OILS

		Kinematic Viscosity (Centistokes)		
		0° F.		
210° F.	100° F.	*A*	*B*	*C*
5	30.90	1,431	1,480	1,478
6	40.62	2,235	2,285	2,280
7	51.21	3,292	3,300	3,293
8	62.58	4,561	4,536	4,525
9	74.69	6,083	6,006	5,991
10	87.50	7,871	7,720	7,701
12	115.1	12,203	11,920	11,895
14	145.0	17,595	17,212	17,156
16	177.2	24,154	23,661	23,581
18	211.6	31,996	31,326	31,244
20	247.8	41,086	40,266	40,136
22	285.9	51,207	50,534	50,356
24	325.9	62,901	62,179	61,980
26	367.6	75,876	75,244	75,022
28	410.9	90,247	89,780	89,514
30	455.6	105,900	105,820	105,440
32	502.0	123,130	123,410	122,970
34	549.9	141,960	142,600	142,100
36	599.2	162,010	163,400	162,830
38	649.9	183,760	185,870	185,220
40	702.0	207,010	210,040	209,310

Viscosity ratios at 400° F. (204.4° C.) for oils matched as to viscosity at 0° F. (−17.8° C.) might also be developed in a manner similar to that used in establishing the zero viscosity factor. It appears that such a relation would be valuable in further establishing the viscosity-temperature characteristics of lubricating oils through relatively simple and useful means.

ACKNOWLEDGMENT

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A Practical Method for Determining Hiding Power of Paints

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A METHOD for the determination of hiding power of paints which would be readily adaptable to practical use in the paint industry has been sought for some years.

In developing the method presented in this paper, consideration has been given to the requirements which should be met by a practical hiding-power test. It was assumed to be desirable that (1) a single coat of paint at an approximately normal spreading rate should be sufficient; (2) the hiding-power values should be obtainable from either a wet or dry film, and should give independent numerical values without reference to another paint or pigment; (3) the background should be visually obliterated; and (4) the effect of the ultimate brightness of the paint should be minimized.

A method complying with these requirements would represent an advance over most visual obliteration methods thus far developed, which are subject to one or more of several limitations—for instance, the necessity of multiple coatings, indefiniteness of end point, basing of results on observation of wet films, and particularly lack of consideration given to the effect of ultimate brightness of the paint. These limitations are inherent, not only in those methods which use a black and white contrast background, but also in those involving gray and white, if complete visual obliteration is used for the end point.

Recently several methods have been developed which make use of the above-mentioned contrasts, but paint is applied to only partial obliteration of the background. There are objections to the method developed by Bruce (*1*), because of its inflexibility and because of the expensive equipment necessary.

Sawyer (*10*), on the other hand, has obtained hiding-power values on a more practical basis, by the partial obliteration of a gray and white background interpreted in terms of a comparison standard which has been evaluated for complete hiding over the same background. Although the partial obliteration method will give comparative values for very similar paints, correct evaluation by visual observation is difficult in the case of a gloss paint having a low pigment concentration in comparison with a flat paint of high pigment concentration. Sawyer (*11*) simplified his original method by making several paint-outs of increasing thickness and calculating the contrast ratio of each painted chart. Thus by obtaining several points he was able to draw a contrast-ratio film-thickness curve from which he obtained relative hiding-power values for paints or pigments for a chosen contrast ratio.

These methods are time-consuming and the paint industry is interested in obtaining a more simple method. Therefore, the development of a new and practical hiding-power method was undertaken.

Method

Paint is applied by brushing in a practical manner over a contrast background consisting of black (approximately 5 per cent brightness) and gray (25 per cent brightness). The end point is reached when the obliteration of the contrast is just complete to the eye. Some care must be exercised in order not to go beyond the end point, and it may be advisable for an inexperienced operator to make severa paint-outs in order to obtain a check.

In the observation of the panel some standard light source is advisable. It has been found that satisfactory results are obtained when the paint-out is held at arms' length and in north light. The test can be made on a wet or dry basis, as the particular case warrants.

In the case of flat paints or paints which contain a considerable percentage of volatile, it is advisable to make two or possibly three brush-outs in order to obtain a satisfactory end point, because of a change in hiding as the film dries.

The simple weighing of the panel (or weighing of the brush and of the can of paint) before and after painting permits an easy calculation of the hiding power in desired terms.

In the development of this hiding-power method, a study of obliteration curves of paints was made, like the curves obtained by Haslam (*4*), by applying a paint uniformly over a chart composed of black and several intermediate grays approaching a white. The paint was applied by brushing uniformly and the resulting brightness increase measured. The brightening power of the paint over each gray undersurface

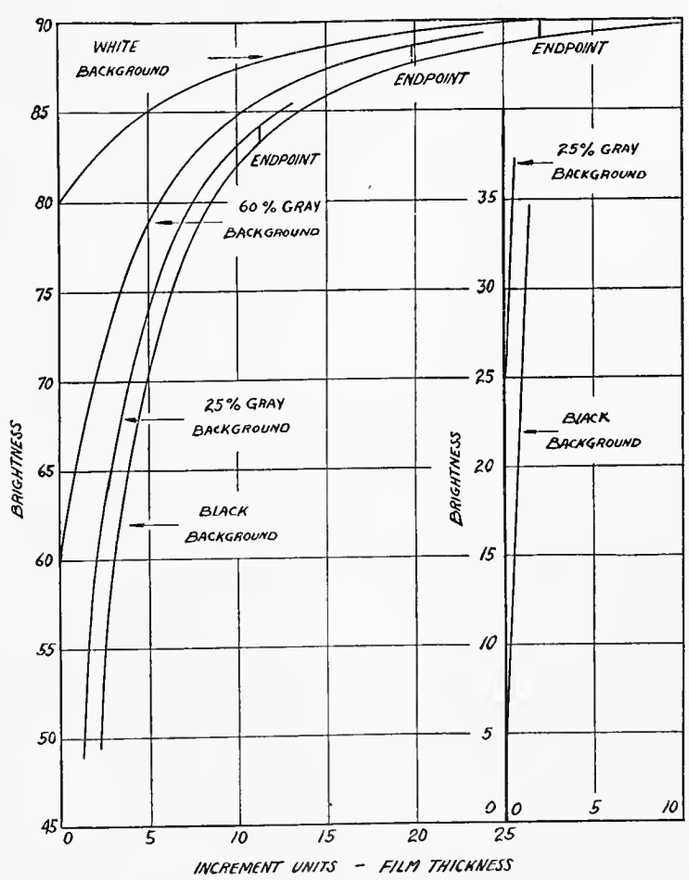

Figure 1. Visual Contrast Obliteration

Black–25 per cent gray; black–60 per cent gray; and black–white

was studied. These data were compiled and a brightness obliteration curve for the paint was obtained. Although curves of this type are of little value for practical use, they furnish the means of studying the rates of change in brightness with change in film thickness.

Let us consider a background composed of gray and black squares over which small amounts of white paint are applied successively and uniformly over both surfaces. Some point will be reached at which the darker surface approaches the original brightness of the lighter of the two undersurfaces, but at the same time an equivalent amount of paint is being applied to the lighter contrast surface. The result is that the brightness of the lighter surface also increases, but to a relatively less degree than that of the darker surface. If the application of the paint is continued, at some point complete visual obliteration of the contrast will result.

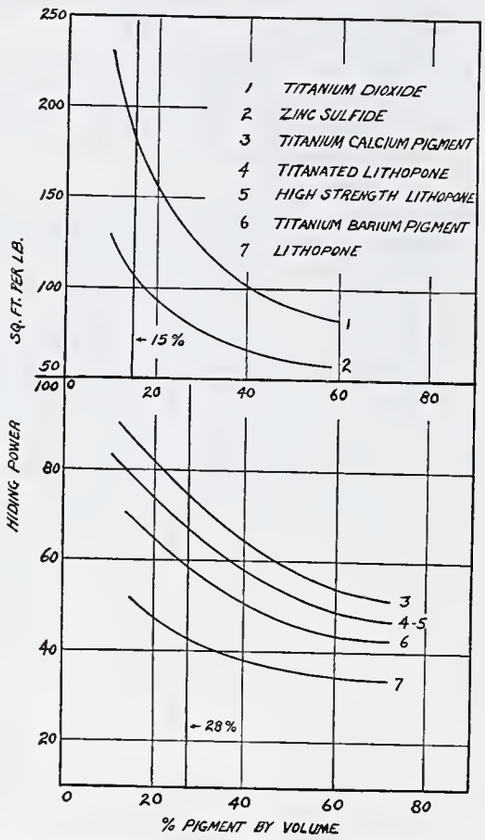

Figure 2. Pigment Hiding-Power Values for Change in Pigment Concentration

The end point will vary with the contrast background used. Figure 1 shows a series of curves for three contrast backgrounds—black and 25 per cent gray, black and 60 per cent gray, and black and white (80 per cent). Assuming the contrast sensitivity of the eye as 1 per cent, the respective end points (at just visual obliteration) for the three backgrounds used are indicated on the graphs. (Kraemer and Schupp, *5*, showed that in the case of a checkerboard design, the average person can just distinguish a contrast of slightly less than one per cent. Experimentally the authors have found this to be correct.) It will be observed that the visual contrast obliteration takes place in the case of a black and 25 per cent gray background in the region where a comparatively small increment of paint (about 1 unit) is required to obtain a 1 per cent increase of brightness; in the case of a black and 60 per cent gray background the visual obliteration is in the region where about 3 units of paint increment are required for 1 per cent increase in brightness; in the case of a black and 80 per cent white background, almost 10 units of paint increment are required to obtain 1 per cent increase of brightness in the region of the curve where visual contrast obliteration takes place.

In consideration of these factors a chart having a checkerboard area of one square foot was adopted upon which are printed alternate black (5 per cent) and gray (25 per cent) squares of approximately 2 × 2 inches, surrounded by a 0.375-inch border of the gray and an outer border of white.

By means of the method developed it has been possible to determine hiding-power values at visual obliteration for a number of paints and also to demonstrate in a practical manner some of the factors which affect hiding-power values.

Factors Influencing Hiding-Power Values

Among the factors of importance is the role that the pigment volume concentration plays in a paint film. Pfund (*7*) states, "The dilution effect is observed when hiding-power measurements are carried out on mixtures whose pigment-vehicle ratio is varied through wide limits. It is found that unit mass of the pigment will hide increasingly greater areas as the pigment-vehicle ratio is decreased." Sawyer (*10, 11*) also gives some data in support of this conception.

In order to show the effect of pigment concentration on the hiding power of paints and at the same time to compare hiding-power values of a series of paints, using the method described in this paper, a number of pigments were ground into pastes with linseed oil (containing drier) and mineral spirits (added to facilitate grinding of pastes of high pigment concentration; the exact amount remaining in the paste was determined by analysis). The following pigments were used: lithopone, titanium barium pigment, high strength lithopone, titanated lithopone, titanium calcium pigment, zinc sulfide, and titanium dioxide. In order to obtain paints of brushing consistency and of the desired pigment-vehicle ratios the pastes were diluted with oil or volatile in whatever proportion was necessary.

Figure 2 shows the hiding-power curves obtained for dry films of the various pigments at different pigment concentrations. In all cases, the hiding power per unit of pigment increased as the pigment concentration decreased.

In the consideration of a hiding-power method the factor of spreading rate plays a part; a method to be practical should employ an approximately normal spreading rate. This feature has been studied in connection with the method described in this paper and it has been found that the authors' method permits hiding-power determinations at spreading rates very close to those of practical application. Table I gives spreading rates at various pigment volume concentrations, based on observations of dry films.

Table I. Spreading Rates

(Square feet per gallon)

Volume Concentration	Lithopone	Titanium Barium Pigment	Titanated Lithopone and High-Strength Lithopone	Titanium Calcium Pigment
20	340	460	530	440
30	450	600	700	580
50	630	830	930	790
70	830	1070	1170	970

Volume Concentration	Zinc Sulfide	Titanium Dioxide
10	430	720
20	630	930
30	800	1170
40	900	1300
50	1060	1460
60	1200	1650

As the pigment volume concentration increases the resulting spreading rate of paint increases. This is natural because an increase in pigment content of the paint decreases the relative amount necessary for hiding. The hiding-power spreading rate for the abnormal pigment volume concentration paints should not be confused with the practical pigment volume spreading rate paints. Paints between 20 and 30 per cent pigment volume concentration are practical gloss-type paints and paints of 50 to 70 per cent pigment volume concentration (in the dry film) are usually flat paints. There is generally a high percentage of volatile in flat paints; this is equivalent to a reduction in actual spreading rate (on pigment basis), thus approaching a rate more consistent with painting practice. In the case of zinc sulfide and titanium dioxide paints, a practical pigment volume concentration of between 10 and 20 per cent is within the range of ordinary use.

In case of a complete obliteration method as described in this paper, a decrease in the ultimate brightness of a paint results in higher hiding-power value figures, as observed at visually complete contrast obliteration. This effect of decreased brightness has been previously demonstrated by Pfund (*8*), Gardner (*2*), and Rhodes and Fonda (*9*). Morrison (*6*) found that there was an increase in the hiding power of a paint when raw linseed oil was substituted for refined linseed oil. This was ascribed by him to the presence of coloring matter in the raw oil; obviously it was due to the decreased brightness of the paint.

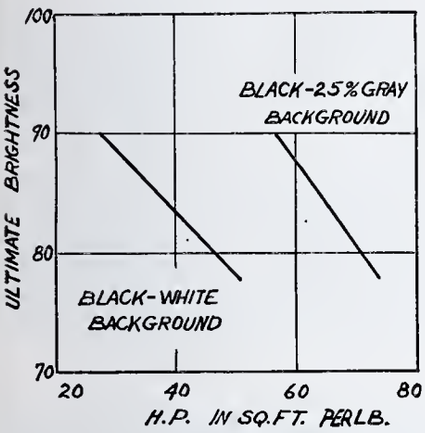

Figure 3. Increase in Hiding Power with Decrease in Brightness

The interdependence of brightness of a paint and its hiding value is illustrated in Figure 3. A practical linseed oil paint of 90 per cent ultimate brightness was reduced in brightness successively to 84 and 78 per cent by the addition of a coloring material (black). The paints thus obtained were tested for complete hiding on Gardner's black and white checkerboard chart, and also by the method developed by the authors. The black and gray (25 per cent) background considerably minimizes the effect of brightness on hiding value in comparison with the black and white background. Thus in the latter case there is approximately 7 per cent increase of hiding value for 1 per cent decrease in brightness of the paint, whereas if black and 25 per cent gray background is used there is an increase of only 3 per cent (approximately) of hiding value for 1 per cent decrease of brightness.

Another factor which may influence hiding-power values is the effect of pigment concentration in the film on the ultimate brightness of the paint. Although this influence can be clearly traced even at comparatively low pigment concentrations, it manifests itself in a most pronounced manner when the pigment concentration (of most pigments) reaches about 50 per cent by volume. From this point the increase in brightness is very rapid. This high pigment concentration covers the range of flat paints. Figure 4 illustrates the relation between pigment volume concentration and brightness of the dry film.

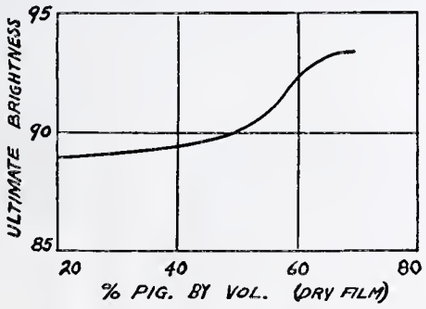

Figure 4. Increase in Brightness with Pigment Concentration

It should therefore be expected that the hiding values would be decreased at higher pigment concentrations; there is, however, no evidence of this effect in results obtained on a black and 25 per cent gray background. No definite explanation of this phenomenon can be given at this time; but Sawyer's assumption (*10*) of a more opaque film produced by increased pigment packing appears to be reasonable.

Evaluation of Pigments from Hiding-Power Values

For the purpose of comparison, hiding values of paints of 28 per cent pigment volume concentration were selected for composite pigments because this concentration is considered standard in pigmentation of most linseed oil paints. On the other hand, zinc sulfide and titanium dioxide are used at low pigment concentration only, and were therefore compared on the basis of 15 per cent pigment volume concentration.

Hiding-power values determined by the authors are as follows (Figure 2):

Table II. Hiding-Power Values

28 Per Cent Pigment Volume Concentration	Hiding Power
	Sq. ft./lb.
Lithopone	43
Titanium barium pigment	58
High-strength lithopone	67
Titanated lithopone	67
Titanium calcium pigment	74
15 Per Cent Pigment Volume Concentration	
Zinc sulfide	108
Titanium dioxide	180

Hiding-power values at pigment concentrations other than those given above may be readily obtained by drawing a vertical line through hiding-power curves at any desired pigment concentration. (It is interesting to note that the hiding-power relations of various pigments shown above are consistent with those obtained by Hallett, *3*.)

Acknowledgment

Acknowledgment is due to Jos. L. Turner, director of research, and D. W. Robertson, sales engineer, both of the Titanium Pigment Co., Inc., for their valuable help and suggestions in the preparation of this paper.

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Starch from Waste Sweet Potatoes May Find Use in Paper Industry. According to the results of experimental tests made by the Bureau of Standards, sweet potato culls offer some possibility as a source of starch for sizing paper and for paper adhesive. The culls constitute a huge waste in the southern states, and the Bureau of Standards and the Bureau of Chemistry and Soils are jointly endeavoring to find ways of profitably using them.

Corn starch and cassava starch are used extensively in book papers to improve their printing quality. The Bureau of Standards made and tested wood-fiber book papers sized with these starches and with sweet potato starch and the latter compared very favorably with the others.

Specific Refractive Dispersion as a Method for Distinguishing between Different Series of Hydrocarbons

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THE analysis of hydrocarbon mixtures is a difficult problem for which there are no satisfactory methods that are both simple and generally applicable. The experience of this laboratory has been that in general a combination of physical and chemical methods is more satisfactory than either type alone. Among the physical methods that have proved of value is one employing specific refractive dispersion. Dispersion is the difference in refractive indices determined for light of two different wave lengths; specific dispersion is dispersion divided by density, both constants being determined at the same temperature. In order to express specific dispersion as a convenient whole number, it is multiplied by some power of 10. As employed in this paper, specific refractive dispersion equals

$$\frac{n\lambda_1 - n\lambda_2}{d} \times 10^4 \text{ or } \frac{\Delta n}{d} \times 10^4$$

Most of the classical work on the various aspects of refractivity has been concerned with molecular refractivity. This property is of value in establishing the purity or the structure of a compound, but it is not very suitable for the analysis of hydrocarbon mixtures. Waterman (*19*, *22*) and his co-workers have used the specific refraction formula of Lorentz-Lorentz, $\frac{N^2 - 1}{N^2 + 1} \times \frac{1}{d}$, for hydrocarbon analysis.

Several expressions for dispersion have also been used in work on the structure of compounds, but for some reason relatively few serious attempts have been made to employ specific dispersion in hydrocarbon analysis. The most interesting recorded attempts were made by Darmois (*6*), Dixmier (*7*), Mutte (*14*), Cortot (*8*), and Waterman and Perquin (*21*).

Cortot's work was confined to a limited number of cyclic hydrocarbons. Mutte and Dixmier used specific dispersion for the *g* and *D* lines. Waterman and Perquin employed dispersion directly and also the rather unusual expression $\frac{nG - nC}{nD - 1} \times 10^4$. The latter expression does not appear to have as great value as one that includes density. Darmois published constants for the specific dispersion of six series of hydrocarbons. They are apparently intended to be used only for light gasolines since his value for the aromatics appears to have been based on benzene, toluene, and xylene only. The higher aromatics have considerably lower dispersions.

Experimental

The densities and refractive indices of a number of hydrocarbons and hydrocarbon mixtures were determined, the densities by comparing the specific gravity of the sample at 20° C. with water at 4° C. using a Westphal balance, and the refractive indices with a Pulfrich refractometer which had been calibrated as described below. Values were determined at 20° C. for the following five spectrum lines:

Line	Wave Length
	Å.
C (Hα)	6563
D	5893
e (Hg green)	5461
F (Hβ)	4861
g (Hg blue)	4358

The *D* line was supplied by a sodium lamp. The *C* and *F* lines were supplied by a Geissler discharge tube containing hydrogen. The *e* and *g* lines were supplied by a Geissler tube having aluminum electrodes and having a small amount of mercury in each bulb. In each case, instead of using a closed evacuated Geissler tube, an open tube was employed. The tube was connected with a vacuum pump and also with an automatic electrolytic hydrogen generator. When the tube was in use the vacuum pump was run constantly and just sufficient hydrogen was admitted to give the brightest illumination.

It was impossible to employ the commonly used *G'* (4340 Å.) line, because with the equipment available the line was not sufficiently brilliant for accurate measurements. For this reason the *g* line was substituted. The addition of mercury

Table I. Summary of Refractive Indices and Dispersions of Different Hydrocarbons

Sample No.	Substance	Refractive Indices at 20°					Dispersions × 10^4	
		C	*D*	*e*	*F*	*g*	*F* − *C*	*g* − *C*
1	*n*-Hexane	1.3743	1.3762	1.3772	1.3809	1.3848	66	105
9	Decane (2,7-dimethyloctane)	1.4069	1.4092	1.4104	1.4146	1.4185	77	116
11	Trimethylethylene	1.3860	1.3883	1.3903	1.3945	1.3983	85	123
12	Octylene	1.4115	1.4138	1.4159	1.4204	1.4252	89	137
14	Diamylene	1.4336	1.4363	1.4378	1.4426	1.4475	90	139
15	Decene[a]	1.4227	1.4255	1.4268	1.4315	1.4363	88	136
17	Triamylene	1.4503	1.4532	1.4548	1.4598	1.4652	95	149
18	Hexadecene	1.4393	1.4428	1.4441	1.4487	1.4538	94	145
20	Decadiene	1.4356	1.4387	1.4404	1.4459	1.4519	103	163
21	Benzene[a]	1.4967	1.5014	1.5049	1.5137	1.5237	170	270
22	Toluene[a]	1.4922	1.4966	1.5000	1.5081	1.5180	159	258
23	Ethylbenzene[a]	1.4912	1.4955	1.4987	1.5065	1.5155	153	243
24	*m*-Xylene[a]	1.4931	1.4975	1.5009	1.5089	1.5184	158	235
25	Mesitylene (1,3,5-trimethylbenzene)[a]	1.4920	1.4962	1.4995	1.5074	1.5163	154	243
26	Diethylbenzene[a]	1.4934	1.4974	1.5004	1.5080	1.5169	146	235
27	1,2,4-Dimethylethylbenzene[a]	1.5003	1.5046	1.5077	1.5153	1.5246	150	243
28	*p*-Cymene	1.4867	1.4906	1.4936	1.5011	1.5097	144	230
29	Triethylbenzene[a]	1.4952	1.4990	1.5024	1.5090	1.5179	138	227
30	α-Phenyl-α-butene[b]	1.5200	1.5249	1.5292	1.5381	1.5517	181	317
31	Hexahydrobenzene	1.4241	1.4263	1.4276	1.4319	1.4362	78	121
32	Hexahydrotoluene	1.4220	1.4243	1.4256	1.4299	1.4343	79	123
33	Hexahydro-*p*-cymene	1.4362	1.4387	1.4400	1.4442	1.4489	80	127
34	Decahydronaphthalene	1.4737	1.4765	1.4779	1.4825	1.4876	88	139
35	Dehydrobenzene	1.4744	1.4783	1.4813	1.4884	1.4975	140	231
36	Dihydro-*p*-cymene [*p*-menthadiene-(1,3)]	1.4779	1.4815	1.4841	1.4906	1.4983	127	203
37	Tetrahydrobenzene	1.4548	1.4576	1.4593	1.4644	1.4706	96	158
38	1,2,3,6-Tetrahydrotoluene	1.4545	1.4574	1.4593	1.4645	1.4704	99	159
39	Tetrahydro-*p*-cymene (*p*-menthene-3)	1.4555	1.4584	1.4599	1.4650	1.4707	95	152
41	Pinene	1.4663	1.4694	1.4711	1.4764	1.4823	101	160
42	1,2-Dihydronaphthalene[a]	1.5685	1.5748	1.5798	1.5913	1.6058	228	373
43	1,2,3,4-Tetrahydronaphthalene[a]	1.5385	1.5433	1.5468	1.5552	1.5655	167	270
45	Dipentene	1.4747	1.4784	1.4805	1.4866	1.4936	119	189
47	Indene	1.5655	1.5719	1.5769	1.5887	1.6028	232	373

[a] Values are averages of determinations made with two prisms.
[b] Readings affected by action of light on samples.

Table II. Summary of Physical Constants

Sample No.	Substance	B. P. at 760 mm. ° C.	Density at 20°	n_D^{20}	$\frac{nF - nC}{d} \times 10^4$	$\frac{ng - nC}{d} \times 10^4$
	PARAFFINS					
1	n-Hexane	68.9	0.6602	1.3762	100	159
9	Decane (2,7-dimethyloctane)	159.9	0.7240	1.4069	106	160
	IMPURE PARAFFINS FROM PETROLEUM					
3	Nonane	149.9	0.7323	1.4136	98	159
5	n-Decane	172.1	0.7500	1.4200	101	156
5-A	n-Decane after 7 SO_2 treatments	171.0	0.7415	1.4172	100	156
8	Decane (2,7-dimethyloctane)	161.5	0.7477	1.4176	100	156
10	Dodecane and tridecane mixture	221.3	0.7843	1.4348	101	162
	OLEFINS					
12	Octylene	123.2	0.7217	1.4138	122	187
14	Diamylene	156.4	0.7682	1.4363	116	181
15	Decene	160.4	0.7418	1.4255	119	183
17	Triamylene	248.0	0.8087	1.4532	117	184
18	Hexadecene	285.9	0.7848	1.4503	120	184
	DIOLEFIN					
20	Decadiene	162.8	0.7629	1.4387	135	214
	AROMATICS					
21	Benzene	80.26	0.8807	1.5014	193	307
22	Toluene	110.8	0.8677	1.4966	183	297
23	Ethylbenzene	135.8	0.8682	1.4955	178	280
24	m-Xylene	139.8	0.8661	1.4975	182	292
25	Mesitylene	164.0	0.8628	1.4962	178	282
26	Diethylbenzene	181.8	0.8640	1.4974	169	272
27	1,2,4-Dimethylethylbenzene	187.6	0.8792	1.5046	171	277
28	p-Cymene	176.6	0.8582	1.4906	168	268
29	Triethylbenzene	217.4	0.8655	1.4933	160	262
	AROMATIC OLEFIN					
30	α-Phenyl-α-butene	197.1	0.8927	1.5249	203	355
	SATURATED NAPHTHENES					
31	Hexahydrobenzene	81.0	0.7781	1.4263	100	156
32	Hexahydrotoluene	100.8	0.7707	1.4243	102	160
33	Hexahydro-p-cymene	168.4	0.7950	1.4387	101	160
34	Decahydro naphthalene	192.4	0.8895	1.4765	99	156
	UNSATURATED CYCLICS, TWO DOUBLE BONDS					
35	Dihydrobenzene	85.0	0.8417	1.4783	166	274
36	Dihydro-p-cymene [p-menthadiene-(1,3)]	177.2	0.8502	1.4815	149	239
	UNSATURATED CYCLICS, ONE DOUBLE BOND					
37	Tetrahydrobenzene	82.4	0.8417	1.4576	114	187
38	1,2,3,6-Tetrahydrotoluene	103.4	0.8010	1.4574	124	198
39	Tetrahydro-p-cymene (p-menthene-3)	168.0	0.8098	1.4584	117	189
41	Pinene	156.5	0.8578	1.4694	116	187
	HYDROGENATED NAPHTHALENES					
42	1,2-Dihydronaphthalene	211.0	0.9943	1.5748	230	375
43	1,2,3,4-Tetrahydronaphthalene	207.0	0.9708	1.5433	172	278
34	Decahydronaphthalene	192.4	0.8895	1 4765	99	156
	MISCELLANEOUS					
45	Dipentene	176.2	0.8512	1.4784	140	222
47	Indene	...	0.9816	1.5719	236	380

to a Geissler tube offers a simple and easy method of obtaining the two mercury lines. The *e* line offers no particular advantage because its wave length is between the wave lengths of the easily obtainable *D* and *F* lines. The *g* line is of distinct value since its wave length is almost as low as the *G* line. The only disadvantage in its use is the necessity of calculations to make values obtained with it comparable to those obtained with the *G* line. However, the closeness of the two wave lengths permits such calculations to be made without introducing significant errors.

Calibration of Refractometer. Suitable precautions to insure accurate readings included the use of apparatus to supply the water jacket of the refractometer with water at a constant temperature. The instrument is supplied with two prisms to permit determinations to be made over a wide range and, wherever possible, both prisms were used and the results averaged. The zero point of the instrument was determined by the method described by Firth (*13*). Corrections for the zero point were made for each prism. In addition, to calibrate the instrument, determinations of the refractive indices of six substances were compared with determinations made by the classical angle of minimum deviation method by J. W. Barnes.

The substances used, which were selected to give a wide range of refractive indices, included water, *n*-propyl alcohol, chloroform, methyl salicylate, oil of cassia, and monobromonaphthalene. Barnes' measurements were taken as standard and by comparing the results the following sets of corrections were obtained for the two prisms of the Pulfrich:

Spectrum Line	Prism 1	Prism 2
C	−0.00040	−0.00037
D	−0.00055	−0.00038
e	−0.00050	−0.00030
F	−0.00048	−0.00022
g	−0.00050	−0.00020

Experimental Results. The refractive indices and dispersions, both at 20°, for a number of hydrocarbons are summarized in Table I. The more important specific dispersions together with the boiling points, densities, and refractive indices for the *D* line are summarized in Table II. The boiling points represent the temperature reading when 50 per cent of a 100-ml. sample had distilled over (A. S. T. M. D-216). The boiling points were determined when the atmospheric pressure was within 5 mm. of 760 mm. and were corrected to 760 mm.

All the hydrocarbons for which constants are given were prepared or purified in this laboratory, and most were highly purified products. In some cases they were mixtures of isomers, the separation of which was impossible by ordinary methods. They were considered to be sufficiently pure for work of this character.

In Table II the values for a group of impure paraffins separated from petroleum are included. These are believed to be of interest because they prove that the difficulty in purifying paraffins from petroleum is due to presence of naphthenes and demonstrate the impossibility of separating naphthenes and paraffins by the chemical methods normally employed in analyzing hydrocarbon mixtures.

The literature is full of physical constants of hydrocarbons isolated from petroleum and considered pure by the men who isolated them. The work of Washburn and his associates at the Bureau of Standards has demonstrated that although it is possible to isolate pure hydrocarbons by special physical methods, the vast majority of hydrocarbons previously isolated have been grossly impure.

Shepherd, Henne, and Midgley (*17*) starting with a petroleum mixture, 70 per cent of which consisted of normal paraffins, isolated some pure individual paraffins with the aid of chlorosulfonic acid. Whether their success was due to the purity of the starting material or to the long treatment with the particular reagent used, the fact remains that practically all attempts to separate pure paraffins by chemical treatment have failed.

Samples 3, 5, and 8 were from fractionated Pennsylvania petroleum. They had been washed with fuming sulfuric acid; treated three times with nitrating acid; washed with caustic soda, water, and methyl alcohol; washed twice with ten volumes of liquid sulfur dioxide and again with caustic soda and water; and finally distilled over sodium. Sample 5-A was given an additional five washings with ten volumes of liquid sulfur dioxide and was frozen, filtered with suction, and separated from the hydrocarbons of lower melting point. After the fifth washing with liquid sulfur dioxide, further washings continued to dissolve a portion of the sample without affecting its density or refractive index, and the principal effect of the freezing treatment was to remove some 2,7-dimethyloctane from the normal decane which constituted the bulk of the sample.

After these treatments, the densities and refractive indices of the samples were much lower than the values obtained after the original fractionations, but were still larger than the values for synthetic paraffins by 1 or 2 $\times 10^{-2}$. The data show that the hydrocarbons resisting the strenuous chemical treatment were naphthenes, since an increase in density caused by other hydrocarbons would have increased the specific dispersion.

Literature Values

The experimental work summarized in Tables I and II was completed a number of years ago. At that time, in order to supplement the determined values with data for a longer number of hydrocarbons than it was expedient to prepare, a search of the literature was made for density and refractive index determinations of synthetic hydrocarbons, from which specific dispersions could be calculated. A complete list of the references would be too long for inclusion here, but a number of the more valuable ones are given (*1–5*, *9*, *11*, *15*, *16*). Numerous values were also obtained from Landolt and Börnstein, International Critical Tables, and particularly the monumental work of Eykmann which was collected and published in 1919 by the Hollandsche Maatschappi. Two more recent sets (*10*, *18*) of values for paraffins have been added to the literature values, but do not change the older averages.

In general, the usefulness of literature data is limited by the fact that only a comparatively few investigators have reported densities and indices at the same temperature. Where there was a difference of only a few degrees, temperature corrections were made; otherwise the data were not used. Values that were obviously erroneous were also omitted. In calculating specific dispersion, refractive indices for the g line were obtained from curves by plotting wave lengths against indices where values for the G' line were available. The difference in the index for the g and G' lines is so small that the errors as a result of using the curves are negligible.

The values determined experimentally are compared with a summary of the literature values in Table III. Representative values, given for the more important series of hydrocarbons, are the approximate averages of the two preceding columns and are believed to be suitable for use on unknown mixtures. For reference, Darmois' values are included.

Table III. Summary of Specific Dispersions of Different Series of Hydrocarbons

Type of Hydrocarbon	$\frac{nF - nC}{d} \times 10^4$ Literature	$\frac{nF - nC}{d} \times 10^4$ Determined	$\frac{ng - nC}{d} \times 10^4$ Calculated from literature	$\frac{ng - nC}{d} \times 10^4$ Determined	$\frac{ng - nC}{d} \times 10^4$ Representative	$\frac{G' - C}{d} \times 10^4$ Darmois
Saturated aliphatics (paraffins)	97	103	154	159	157	155
Saturated cyclics (naphthenes)	98	101	155	158	157	151
Unsaturated aliphatics with one double bond (olefins)	120	119	186	184	185	194
Unsaturated cyclics with one double bond	119	116	183	190	185	191
Unsaturated aliphatics with two double bonds (diolefins)[a]	142	131	222	214	...	250
Unsaturated cyclics with two double bonds	157	159	246	256	250	...
Unsaturated aliphatics with two conjugated double bonds[a]	222	...	375	...	...	...
Unsaturated cyclics with two conjugated double bonds[a]	184	...	298	...	...	...
Saturated cyclics with one double bond in side chain	125	...	201	...	...	...
Unsaturated cyclics with one double bond in side chain	135	...	214	...	...	...
Aromatics	...	...	(See Figure 1)			305
Aromatic olefins with one double bond	204	219	355	356	...	...

[a] Too few values are available.

Discussion of Results

It is known that for certain classes of organic compounds differences in structure affect dispersion. For example, Eykmann (*12*) has shown that differences in the distances of side-chain double bonds from the nucleus causes differences in the dispersion of safrole and eugenole compared to isosafrole and isoeugenole, respectively. The object in summarizing a large number of literature values, in addition to the determined values, was to establish generalizations as free as possible from the influences of differences in structure. It was hoped that the hydrocarbons likely to be encountered in practical work would in general correspond to the average values of their class. The discussion below is limited to specific dispersion for the $g-C$ lines which is more useful than the smaller value for the $F-C$ lines.

Saturated Hydrocarbons. The values for paraffins and naphthenes are too close together to permit distinguishing between them. This is evident both from Table III and from the data for the paraffins from petroleum summarized in Table II.

In the case of paraffins there was no variation that could be ascribed to molecular weight or structure, the deviations being irregular and properly ascribed to experimental error. This is also true of cyclics with a six-membered ring. A total of 23 literature and three determined values were within ±4 of 157. This value is also reasonably accurate for a wide variety of other cyclics ranging from dimethyl cyclopropane to dicyclotridecane.

Unsaturated Hydrocarbons. For olefins with one double bond, the average of 22 literature values was 186. The average of 5 determined values was 184. There was no consistent variation with molecular weight. Although olefins can be readily distinguished from saturated hydrocarbons by this method, they cannot be distinguished from unsaturated cyclics. For the latter with one double bond, the average of 16 literature values for five- and six-membered rings was 183. The average of four determined values was somewhat higher, 190.

Too few values are available to permit safe generalizations for either diolefins or unsaturated cyclics with two double bonds. Three literature values were available in each case, the averages being 222 for the diolefins and 246 for the cyclics. For the former, one determination gave 214; for the cyclics, two determinations averaged 256.

Conjugated double bonds produce a marked exaltation, particularly in the case of aliphatic hydrocarbons. Their presence must be considered in unknown mixtures showing high specific dispersions.

Saturated cyclics with one double bond in the side chain have a higher value than that of cyclics with a double bond in the ring, the average of the values in the literature being 201. On the other hand, unsaturated cyclics with a double bond in both the ring and the side chain, common among the terpenes, have a lower value than would be expected. Literature values for ten of these hydrocarbons averaged 214.

Aromatic olefins give high results, the average of 14 literature values for five hydrocarbons being 355, which happens to check the determined value for phenylbutene. This is a coincidence because the value decreases with increasing molecular weight in a manner similar to that of the aromatics which will be discussed below. The diolefins of this class have very high specific dispersion. The conjugated diolefins have values over 700.

Aromatics. The determined value for benzene was 307. The values for the alkyl benzenes are all lower. Since the substitution of alkyl groups increases the boiling point, it is possible to plot the dispersions of the aromatic hydrocarbons against either their molecular weights or their boiling points.

The boiling point curve is the more useful. Such a curve is shown in Figure 1, and is a composite of about 80 determinations including those determined here.

The purpose of the present paper is to compare the different series of hydrocarbons rather than the effect of individual structure, but in general, it may be stated that the effect of substitution on dispersion is related to its effect in decreasing the benzenoid and increasing the paraffinoid character of the

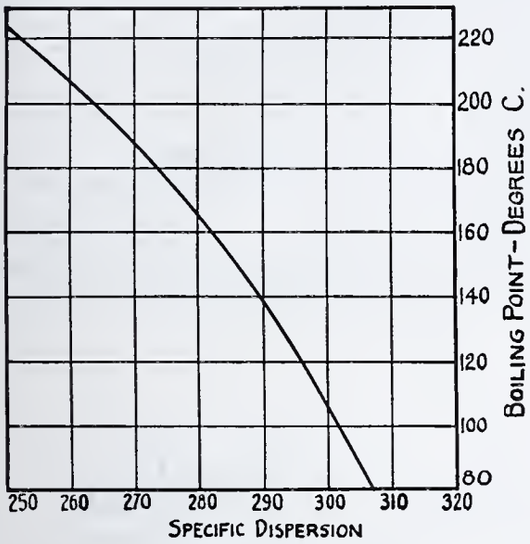

Figure 1. Specific Dispersion of Aromatic Hydrocarbons

hydrocarbon. In other words, the number of carbon atoms, the length of the side chain, and the character of the chain must all be considered. An ethyl group has more effect than two methyl groups, and an isopropyl group has more effect than an *n*-propyl group. The effect tends to decrease slightly with an increase in the number of hydrogen atoms that have been replaced. For aromatics with molecular weights up to 200, the effect of replacing a hydrogen atom with a methyl group varies from 6 to 13.5, with an average of about 8.

Since dispersion of the aromatic hydrocarbons is a constitutive property, it follows that its use in the case of unknown mixtures containing aromatics can never be strictly accurate. However, in many cases the dispersion of the aromatics is so greatly different from that of the other series with which they are mixed that the use of an average curve such as Figure 1 introduces a relatively small error. In other cases, it is possible to make a partial chemical separation that will permit a direct or indirect determination of the dispersion of the particular group of aromatics with which one is dealing.

Naphthalene and Hydrogenated Naphthalenes. The best available averages for these hydrocarbons are:

Naphthalene	490
Δ^1-Dihydronaphthalene	402
Δ^2-Dihydronaphthalene	285
Tetrahydronaphthalene	277
Decahydronaphthalene	156

Use of Specific Dispersion. The possibilities for the use of specific dispersion are varied. Its employment must be governed to a certain extent by the type of hydrocarbon mixture with which one is dealing. It is not the purpose of this paper to discuss the applications of the method in detail, but rather to provide the constants necessary for its use and to indicate which classes of hydrocarbons can, and which cannot, be distinguished by it. The use of the method is frequently indicated when one wishes to confirm or deny conclusions arrived at by other methods. One example of such use may be of interest.

Some time ago this laboratory was engaged in a detailed examination of the condensable hydrocarbons occurring in different types of manufactured gas (*20*). The fractions boiling between 80° and 200° C. are of such a nature that a complete resolution into their constituents is difficult, partly because the ease with which the unsaturated hydrocarbons are polymerized by heat makes it unsafe to submit them to a systematic refractionation.

The only unsaturated hydrocarbons that could be identified as occurring in significant quantities of these fractions are styrene and indene. From a chemical examination, it seemed probable that the rest of the material consisted principally of aromatic hydrocarbons with but a small percentage of naphthenes, paraffins, or other hydrocarbon types present. A previously described (*20*) bromine method was tentatively adopted for the determination of the quantities of styrene and indene present in the different fractions.

It was desirable to confirm the opinion regarding the aromatic character of the material. Also, in view of the nonselective character of the bromine method and of the fact that styrene and indene are found distributed through a number of fractions, it was essential to demonstrate the truth or fallacy of the previous conclusions: (1) that no unsaturated hydrocarbons other than indene or styrene were present in significant quantities; and (2) that the bromine method used actually gave a true picture of the quantities of these hydrocarbons present.

Accordingly, determinations were made of the densities, refractive indices, specific dispersions, and bromine titrations of the different fractions of a number of samples of condensate. The results of this examination of the middle fractions of one sample are given in Table IV.

Table IV

Fraction	Cut ° C.	Density at 20° C.	n^{20}_D	Specific Dispersion $\frac{ng - nC}{d} \times 10^4$	Unsaturation G. bromine/ml.
8	105–108	0.8680	1.4958	293	Trace
9	108–111	0.8657	1.4959	293	Trace
10	111–114	0.8663	1.4957	292	0.0063
11	114–119	0.8655	1.4956	293	0.0125
12	119–129	0.8678	1.4983	304	0.1250
13	129–139	0.8710	1.5048	310	0.2312
14	139–143	0.8780	1.5113	321	0.3675
15	143–147	0.8834	1.5147	343	0.6375
16	147–167	0.8884	1.5191	336	0.6375

Fractions 8 to 11, inclusive, were but slightly unsaturated. The specific dispersions of these fractions were close to those of aromatic hydrocarbons as taken from the boiling point-dispersion curve. The differences indicated by paraffin-naphthene content of from 3 to 5 per cent.

The percentage of styrene in each of the nine fractions was calculated on the assumption that all the unsaturation was due to styrene. The percentage of styrene in each fraction was then calculated from the specific dispersion. (When working with a mixture consisting largely of aromatics and unsaturants with but small quantities of saturated hydrocarbons, approximate values can be obtained by neglecting the small quantities of saturated hydrocarbons. For more accurate values it is necessary to base the calculations on a naphthene- and paraffin-free basis.) The two sets of values are compared in Table V.

Table V

Fraction	Styrene: By bromine %	Styrene: By specific dispersion %
8	Trace	0
9	Trace	0
10	0.5	0.8
11	0.9	0.8
12	9.4	11.1
13	17.3	17.4
14	27.2	26.4
15	47.0	43.0
16	46.7	40.1

The two methods are in excellent agreement on all of the fractions with the exception of 15 and 16. Since fraction 16 was collected above the boiling point of styrene, it was reasonable to expect some other unsaturated hydrocarbon to be present. Indene had been identified. An attempt was made to separate the styrene and indene as far as possible. The results indicated that the quantity of indene present was about two-thirds of that of the styrene. If the results of the two methods are recalculated on this basis, the apparent discrepancy in this case demonstrates the value of the method more closely than do the agreements in the other fractions.

Recalculated, the unsaturation of fraction 16 is

	By Bromine	By Specific Dispersion
	%	%
Styrene	29.2	27.2
Indene	19.5	18.1

Fraction 15 also contained some indene. When the data for this fraction were recalculated to allow for the indene, the results of the two methods were in close agreement.

The results of the two methods on all nine fractions thus fall within recognized experimental errors. It is difficult to conceive of any other hydrocarbon the presence of which is reasonably possible and which has both a bromine value and a specific dispersion equal to that of styrene.

The results obviously demonstrate that the basic material is toluene and higher aromatics; that the bromine method gave a picture of the degree of unsaturation of this material that was accurate within the limits reasonably to be expected in the analysis of hydrocarbon mixtures; and that, aside from some indene, no unsaturated hydrocarbon other than styrene was present in a significant quantity.

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Nature and Constitution of Shellac

IX. Determination of Solubility in Organic Liquids

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Methods for accurate determination of solubilities of resins in organic liquids involve a solvent separation of the resin into its constituents. This paper illustrates how misleading results may be obtained with different procedures unless precaution is taken to eliminate two important sources of error: the tendency of insoluble material to be carried into solution as a colloidal sol and of some of the soluble resin to be occluded by the swollen undissolved portion. Consistency in results is no criterion of the applicability of a method.

In view of the amount of work which has been done on determining the solubility of resins in various solvents, it is unfortunate that more study has not been given to the methods employed (*1, 3*). The lack of careful consideration of the true nature of these substances and the factors which may affect the determination may at least in part account for some of the wide variations in values reported.

Resins belong to a very interesting group of substances which give solutions possessing the properties of both true molecular dispersions and colloidal suspensions. Unless this is clearly kept in mind, confusion is apt to arise with regard to what is meant by the solubility of a resin, and what is measured in quantitatively determining the solubility. Since resins do not give saturated solutions even when their average molecular weights are comparatively small (*2, 5*), we are not dealing with solubility in the classical sense. Even with synthetic resins, a determination of solubility involves several molecular resin species and not single identical molecules such as exist in pure substances. The analyst actually measures the amount of those constituents which are soluble; hence, the so-called quantitative solubility determination involves a separation of resins in exactly the same manner in which the analyst would separate a mixture of two or more totally different species.

Obtaining consistent results by any method is not in itself a criterion for judging the applicability of that method. It can be easily demonstrated that the soluble constituents have a tendency to carry into solution material which would otherwise remain insoluble and which is retained by the solvent as a nonsettling suspension or colloidal sol. Such behavior will explain why resin is sometimes precipitated when solutions are diluted with the same solvent (*1*), as, for example, a concentrated solution of shellac in acetone.

Another source of error in such determinations results from the occlusion of soluble constituents by the insoluble material. Where a complete separation is essential, consistent results can be very misleading. In certain cases the occlusion may just compensate for the loss of insoluble material through colloidal dispersion.

Effect of Method

Unless precaution is taken to eliminate these sources of error in the solubility determination, the values obtained by different methods will not be the same. Five sets of determinations with boiling acetone (Table I) show how the above factors can affect the results.

Table I. Effect of Method on Determination of Solubility

Method	Insoluble Resin
	%
1	6.48–12.5
2	0.93–3.00
3	5.01–5.22
4	4.79–5.23
5	5.00–5.21

1. In the first set of determinations, the procedure followed was the same as that which had been developed for the determination of the "hot alcohol–insoluble in shellac" (*6*), but substituting acetone for alcohol as the solvent. Essentially, this method consists in digesting 5 grams of finely ground shellac with 100 ml. of boiling acetone for half an hour, filtering off the residue through a tared extracted paper thimble, and then extracting with boiling acetone for an hour.

This method works very satisfactorily with alcohol, where the residue consists entirely of inorganic and carbohydrate types of material, but with acetone all of the resin is not dissolved and the insoluble material is highly swollen and gelatinous in character. During digestion there is opportunity for this material to occlude and encase portions of soluble resin which may not be removed even when extracted for a protracted length of time. Furthermore, with uncontrolled agitation during the initial solution of

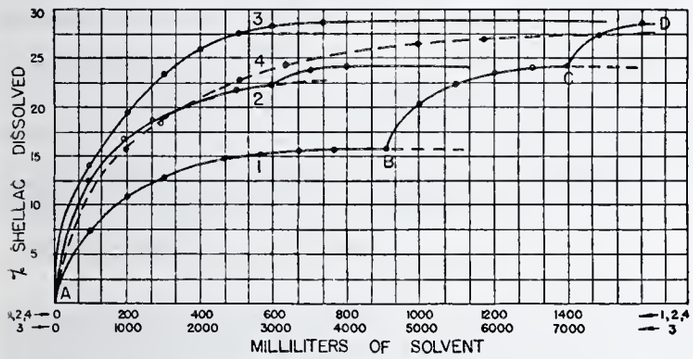

Figure 1. Solubility of Shellac in Diethyl Ether

1. Sample, 10 grams
2. Sample, 5 grams
3. Samples, 5 grams, plus sand, 30 grams
4. Samples, 5 grams (Soxhlet extractor)

the resin, the adsorption by the insoluble portion may not be the same for all determinations. The results given in Table I not only show that inconsistent values were obtained but are also probably higher than the true insoluble constituent content.

2. In the next set of determinations the shellac was admixed with sand, placed in the tared extracted thimble, and extracted directly with a boiling solvent. The addition of sand inhibits the agglomeration of the insoluble resin and permits greater freedom for removal of occluded resin during the extraction.

Although this is not an uncommon type of method for the solubility of resins, no effort is made to control the loss of insoluble material. In fact, conditions in the initial stages favor the passage of not only insoluble resin into the filtrate but also some of the finely divided dirt which is present. Because of the comparatively limited capacity of the siphon tube, the varnishes first obtained can act as a lubricant in the passage of these particles through the filter pores.

Examination of the filtrates from the above determinations showed that such had taken place. On cooling, resin which is insoluble in cold acetone separates out and destroys the colloidal state, so that on reheating to boiling the previously suspended hot insoluble resin and dirt are left as a solid phase and can be readily filtered. The results for these determinations are unquestionably low and it is not surprising that slight fluctuations in each determination would lead to inconsistent results.

3. The study of the filtrates suggested a procedure whereby both sources of error might be minimized. In the third set of determinations, the shellac was digested at the simmering temperature of 54° to 56° C. until the supernatant liquid was practically translucent. The solution was then cooled and reheated nearly to the boiling point as a precautionary step. After decantation of the supernatant liquid, the residue was digested for 10 minutes with fresh solvent, when it was decanted. The beaker containing the residue was then placed on a water bath and the residue broken into small pieces while still moist with solvent. Care was taken during the drying to avoid spattering. When dry it was completely removed with a clean steel spatula, ground in a glass mortar with a glass pestle, and mixed with 25 grams of dry extracted sand. It was then extracted for an hour with boiling acetone.

As can be seen from Table I, consistent results are obtained for duplicate determinations for the first time and these values lie between those of the two previous methods and probably approach very closely the true percentages of insoluble resin.

4. If loss from colloidal suspension was not completely eliminated, we might expect to find some variation in results by using a large sample of shellac. Accordingly 10 grams were digested with 100 ml. of acetone, and within the limits of experimental error the increased size of sample (method 4) had no effect.

5. The procedure was further modified by adding 2 grams of dry, extracted filter-aid to the solution during digestion in order to remove any possible material which would have a tendency to form colloidal suspensions. Here again the results are identical (method 5).

Cold Solvent Extractions

The same sources of error are present in extractions with cold solvents as with boiling liquids and in separations effected by precipitation. In these cases, however, adsorption is more pronounced, as is usually true at lower temperatures, so that the error is likely to be the greater from occluded resin.

The following experiments in this connection demonstrate the fallacy of using the criterion of consistency in results as a standard for judging a method:

Ten grams of finely ground shellac were treated with 100 ml. of pure diethyl ether and allowed to stand for 24 hours. The supernatant liquid was then decanted through a filter paper and the residue treated with a fresh portion of solvent. The weight of resins extracted by each portion was determined after carefully removing the solvent and the results were plotted on coördinate paper. The uniform portion *AB* of curve 1, Figure 1, was obtained. If the swollen residue in the flask is now removed, broken into a fine powder, and then further extracted with ether a second constant value for solubility is obtained. This process can be repeated until most of the occluded resin has been removed. Concordant results will be obtained for duplicate determinations at *B*, *C*, or *D*.

If a larger ratio of solvent to resin is employed, the extraction at each stage will be more complete. This is shown by curve 2, where 5 grams of shellac were used in place of the previous 10-gram quantity. Curve 3 shows the effect of admixture with sand which reduces the coalescence and encasement of soluble material.

The use of a cold solvent extraction apparatus (Figure 2), where the shellac was mixed with sand, gives similar results (curve 4) but in a very much shorter period of time. Even with a large ratio of sand to resin, complete removal of the occluded resin can be had only after a mechanical disintegration of the agglomerates of the residue following the first extraction.

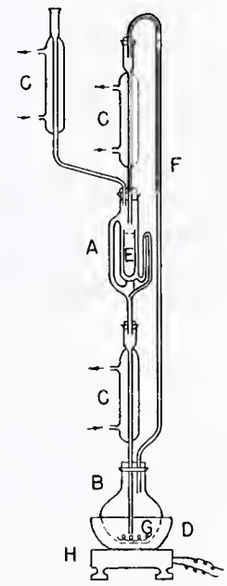

Figure 2. Cold Extraction Apparatus

A. Soxhlet extractor
B. Flask
C. Condenser
D. Water bath
E. Thimble
F. Glass tube, 10 mm. diameter
G. Copper wire
H. Electric stove

In the apparatus shown, the auxiliary condenser was added to prevent escape of ether vapors and to act as a regulator in keeping the internal pressure equal to that of the atmosphere. All connections which were not glass to glass consisted of corks covered with tin foil. This apparatus has the advantage of being constructed from glassware which is usually available in most laboratories.

Applications of Solubility Studies

Accurate data on the solubility of resins in different organic solvents will lead to many interesting conclusions regarding these substances. In many instances the methods employed can be extended to the separation of a resin into its constituent parts and will serve as the key in opening the door to studies of their true constitution (*1*).

In Table II are given values for the true amount of resin which is insoluble in hot acetone in different samples of shellac. Even for the relatively limited number studied, there appears to be some relation between the amount of this resin and the quality and grade of shellac. It is surprising to find that the differences are so marked when the relative amount of insoluble resin is so small. These differences may in part be due to differences in seed-lacs used in the manufacture of the

shellac, and further study may reveal varying amounts as due to season, climatic conditions, and the like as they affect the insect.

Table II. Solubility of Shellac in Boiling Acetone

Sample	Insoluble Resin	Sample	Insoluble Resin
	%		%
T.N.	5.22	U.S.S.A.V.S.O.	3.45
T.N.	7.70	Lemon	1.99
U.S.S.A.T.N. (poor bleaching)	7.44	Lemon	0.26
U.S.S.A.T.N.	4.32	Lemon	0.14

Table III. Comparison of Solubility in Boiling Acetone with Bleaching Quality of Lac

Sample	Insoluble Resin	Excess Bleach Liquor Required
	%	%
D	15.75	54
A	11.62	31
B	10.00	22
E	9.32	19
C	6.91	9
F	4.82	0

Of even greater interest are the results shown in Table III, where the amount of resin insoluble in hot acetone has been determined for the different types of lac which were visually separated from a shellac showing poor bleaching qualities. These samples were described in a previous paper (*4*). A direct relation appears to exist between the amount of insoluble resin and the amount of bleach liquor required to give a definite color of cream in the bleached product. The unextracted resin from hot acetone was in most cases much darker than that which dissolved in this solvent. Any "fixed" coloring matter would probably be found in this insoluble fraction and would account for the poor bleaching qualities. These experiments illustrate the need for a suitable bleaching test (*1*) to be used in the importation of shellac for the express purpose of manufacturing white grades. No complete standardization of white grades can be set up until extensive studies of the bleaching quality of raw lac have been made.

A more complete study is in progress at the bureau, where these methods will be used in conjunction with a wide variety of solvents. Preliminary results show that the varied fractions have different chemical constants (*Kennzahlen*).

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Determination of Sulfide Sulfur in Alkaline Solutions Containing Other Sulfur Compounds

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The various methods for determining sulfide sulfur found in the literature are generally based on either alkalimetric and iodometric titrations alone or in conjunction with precipitation by the addition of salts of some of the heavy metals.

Sutton (*15*) in analyzing a mixture of alkali sulfides, sulfites, thiosulfates, and sulfates, recommends a method worked out by Richardson and Akroyd (*11*) in which the sulfide sulfur is determined by titration with ammoniacal zinc solution. Another method mentioned by Sutton, that of Sander (*12*), involves iodine titration to obtain the total thiosulfate and sulfide sulfur while the thiosulfate sulfur is determined by precipitation with mercuric chloride and titrating the liberated acidity. Griffin (*5*) determines sodium sulfide in black liquor by titration with an ammoniacal zinc solution using nickel ammonium sulfate as outside indicator. For white liquor Griffin recommends Moe's method (*8*) whereby the total sulfide, sulfite, and thiosulfate radicals are determined by iodine titration and the sulfide is precipitated with alkaline zinc chloride. Scott (*14*) determines sodium sulfide by first treating the solution with barium chloride to remove any sulfite present, then distilling the sample with ammonium chloride which will remove the sulfide sulfur in the form of ammonium sulfide. The distillate is collected in ammoniacal cadmium chloride solution, forming cadmium sulfide which is titrated with iodine according to the procedure given for determining sulfur in steel by the evolution method.

Other methods for determining sodium sulfide are those of Budnikoff and Krause (*3*) who oxidize the sodium sulfide with ferric sulfate and titrate the resulting ferrous sulfate with potassium permanganate. Sulfites and thiosulfates will also be oxidized in this procedure. Muller (*9*) determines the sulfur present as sulfide and thiosulfate by titration with iodine solutions, and the thiosulfate alone by acidifying with acetic acid and driving off the hydrogen sulfide by evacuating with a pump. Jarvinen (*7*) precipitates the sulfide with copper sulfate and determines the excess copper colorimetrically. Pauli (*10*) determines the sulfide sulfur in a mixture by titrating the solution with standard iodine solution before and after precipitation of the sulfide with mercuric chloride. Schulek (*13*) boils a solution containing sulfide, polysulfide, and thiosulfate sulfur with boric acid and potassium cyanide whereby the polysulfide sulfur is converted to potassium sulfocyanide, the sulfide sulfur to hydrogen sulfide, and the thiosulfate remains unchanged. Cantoni (*4*) precipitates the sulfide with an excess of potassium arsenite, acidifies the solution, and titrates back the unused potassium arsenite with iodine. Atkin and Hugonin (*1*) treat with lime water and titrate the sulfide sulfur with zinc sulfate, determining the end point by spot tests on lead acetate paper. Horst (*6*) adds the sodium sulfide from a buret to Fehling's copper sulfate solution taken as standard, using sodium sulfide as outside indicator. Billheimer and Reid (*2*) analyze a mixture of sodium hydroxide, sodium sulfide, and mercaptide by determining the total alkalinity to methyl orange, the total reactive sulfur with iodine, and the hydrogen sulfide formed in the decomposition of the mercaptide (by repeatedly boiling the alkaline solution) with a second iodine titration.

Procedure

In the analysis of spent soda solutions used in petroleum refining, it is often necessary to obtain the sodium sulfide content with a fair degree of accuracy, particularly if the treating reactions are being studied. These solutions are strongly alkaline and contain besides sulfates, sulfites, thiosulfates, and sulfides, mercaptides of the type MSR and sulfonates of the type MSO_3R, where M is the alkali

metal used and R an organic radical. The presence of these compounds, particularly the mercaptides, the properties of which are similar to those of the sulfides, greatly complicates the analysis. Thus cadmium, mercury, zinc, and copper salts all form insoluble mercaptides with either or both lower and higher mercaptans. Again, the lower mercaptans are volatile and will be driven off as the ammonium salt together with ammonium sulfide when ammonium chloride is added to the solution. Mercaptides will also react with iodine with the added complication that iodine may combine with the organic group R if the latter happens to be an unsaturated aliphatic.

A procedure has been developed whereby the sulfide sulfur can be determined in an alkaline solution containing sulfates, sulfites, thiosulfates, mercaptides, and sulfonates. The method, while admittedly tedious, has been found to be accurate and has the great advantage that it gives the sulfide content directly.

The procedure depends upon the fact that the lead salts of the above sulfo-acids are all soluble in ammonium acetate, the only exception being lead sulfide. This property of lead sulfide was observed after various experiments with the mercaptides of the heavy metals. The determination is accordingly carried out as follows:

To a known amount of the unknown, such as spent soda solution, add 10 per cent lead acetate solution until no further precipitation takes place. The precipitate will contain, in addition to the lead salts of all the sulfo-acids present, lead hydroxide and the lead salts such as the carbonate and the silicate of some of the impurities generally present in commercial caustic soda. Filter through filter paper and wash with hot water. Unfold the filter over the beaker in which the precipitation had been made and wash the precipitate into the beaker with a stream of hot water. Make the volume up to about 100 cc. with hot water, add 15 grams of solid ammonium acetate and acetic acid until distinctly acid to litmus paper. Boil gently for 15 minutes and filter, washing with hot water. The insoluble portion will consist of lead sulfide together with some lead silicate if sodium silicate was present. For refinery control work filter the ammonium acetate insoluble through a Gooch crucible dried at 105° C. and weigh as lead sulfide, the presence of silica giving somewhat higher results.

For more accurate work, the sulfur content of the lead sulfide precipitate must be determined. For this purpose, filter the ammonium acetate solution through filter paper, wash with hot water, and transfer the precipitate back into the beaker. Oxidize the lead sulfide to lead sulfate by adding bromine or potassium chlorate and nitric acid. Boil off the excess halogen, dilute with hot water, and cautiously neutralize with small portions of solid sodium carbonate, finally adding about 5 grams in excess. Boil for about 10 minutes and let settle. Decant through a filter into a beaker. Add about 25 cc. of 10 per cent sodium carbonate to the insoluble in the first beaker, boil again and filter, washing thoroughly with hot water. The insoluble on the filter will consist of lead carbonate, while the sulfate radical will pass into the filtrate as sodium sulfate. Carefully neutralize with hydrochloric acid, adding a fair excess, evaporate to dryness to decompose nitrates and dehydrate the silica, take up with water and a little hydrochloric acid, and determine the sulfur as usual by precipitation with barium chloride and weighing as barium sulfate.

The method has been tested against known mixtures made up as follows: A standard solution of sodium sulfide was prepared by dissolving about 5 grams of the chemically pure salt in water and making up to 1 liter. The total sulfur was determined in aliquot samples by oxidation with bromine and precipitation with barium chloride. The sulfide sulfur was then determined by the method just described.

According to the writer's experience, low results are sometimes obtained when the total sulfur in a fairly concentrated sodium sulfide solution is determined by adding an excess of bromine to the solution. This is probably due to loss of hydrogen sulfide. For this reason, it is preferable to carry out the oxidation by first adding 4 to 5 grams of sodium hydroxide, then just sufficient bromine to still keep the solution alkaline. In this case the oxidizing agent is sodium hypobromite according to the equation:

$$4NaBrO + Na_2S = Na_2SO_4 + 4NaBr$$

The alkaline solution need only be warmed for one hour for completing the reaction before acidifying with hydrochloric acid and proceeding with the barium chloride precipitation.

Several solutions were made up by using known volumes of the above standard sodium sulfide solutions and adding about equal amounts of the various types of sulfo-salts. The resulting mixtures were then analyzed for their sulfide content, the results being given in Table I.

Table I. Sodium Sulfide Content of Synthetic Mixtures

Solution	Impurities Added	Sodium Sulfide Content: Added	Found	Average	Error
		G./l.	G./l.	G./l.	%
A	None	....	3.5045[a]	3.5028	....
A	Check determination	....	3.5012[a]	....	....
A	None	....	3.4878[b]	3.4827	....
A	Check determination	....	3.4777[b]	....	....
B	Sodium ethyl mercaptide[c]	1.7414	1.7322[d]	....	−0.5
B	Check determination	1.7414	1.7556[d]	....	+0.8
B	Check determination	1.7414	1.7472	....	+0.3
B	Check determination	1.7414	1.7459	....	+0.3
C	Sodium ethyl mercaptide and sodium thiosulfate	1.1648	1.1671	....	+0.2
D	Sodium benzene sulfonate, sodium butyl mercaptide, sodium thiosulfate, and sodium sulfite	0.3483	0.3461	....	−0.2
C	Check determination	0.3483	0.3504	....	+0.2
E	Sodium sulfite, sodium benzene sulfonate and sodium sulfate, sodium ethyl mercaptide and sodium thiosulfate	3.4827	3.4945	....	+0.3
E	Check determination	3.4827	3.4778	....	−0.15

[a] Calculated from total sulfur obtained by oxidation with sodium hypobromite.
[b] Calculated from a sulfide sulfur determination.
[c] Sodium mercaptide solutions prepared by adding 1 or 2 cc. of the pure mercaptans to 100 cc. of a 10 per cent solution of sodium hydroxide.
[d] Data obtained on 10-cc. samples; other determinations made on 50-cc. aliquot portions.

The results obtained on solution A by the bromine–sodium hypobromite method are higher than those obtained on the same solution by the sulfide sulfur method. This is explained by the fact that sodium sulfide always contains other sulfo-salts, particularly sodium thiosulfate, which are oxidized to sodium sulfate by the hypobromite solution. Hence the sodium hypobromite method gives the total sulfur in the sodium sulfide solution which should be equal to (if the salt is pure) or higher than the sulfide sulfur obtained by the method just described. The actual sodium sulfide content of solution A, 3.4827 grams per liter, has therefore been used as a basis for calculating the theoretical amount of sodium sulfide present in the other solutions.

The results show that the presence of other sulfur compounds do not interfere with sodium sulfide determinations made according to the procedure just described and that an accuracy of ±0.3 per cent can be claimed for the method.

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Analysis of Gaseous Hydrocarbons

A Method for Determining Ethylene, Propene, and Butene

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Investigation of unsaturated gaseous hydrocarbons has progressed from total absorption of unsaturates by strong sulfuric acid or bromine water to a method of fractional solution in sulfuric acid in which isobutene is absorbed in 63 to 68 per cent sulfuric acid, propene, and n-butenes by 87 per cent acid, and ethylene in the concentrated acid but with the addition of catalytic agents.

Separation of the gaseous olefins by fractional solution in sulfuric acid seems to have definite limitations in that n-butenes cannot be separated from propene, a fact which is supported by the relative rates of absorption of these olefins by sulfuric acid of various concentrations.

Methods for determining propene and n-butenes by combined low-temperature fractional distillation and sulfuric acid absorption and by analysis of the sulfuric acid solution of the sulfuric acid esters of propene and butene by oxidation to carbon dioxide require, in some cases, relatively large samples of gas and are tedious and time-consuming.

The method described here is dependent upon the fractional solution of propene and butene in 87 per cent sulfuric acid, the density of the mixture of propene and butene serving to give the index, or ratio, of the two olefins. The accuracy of the method has been verified by the analysis of carefully prepared synthetic mixtures of known composition. Application to the analysis of refinery gases has shown the method suitable for rapid, routine analyses.

A DISCUSSION of methods used earlier for determining gaseous olefin hydrocarbons, together with some limitations and inaccuracies of these methods, has been given in an earlier review (*3*).

An oxidation method, based on a procedure used by Tropsch and Dittrich (*1*) for determining the olefins in fractions obtained by low-temperature condensation, was studied first.

Propene and butene were separated from ethylene by 87 per cent sulfuric acid which absorbs the former hydrocarbons without attacking the ethylene. Ethylene was then absorbed in concentrated sulfuric acid activated with nickel and silver sulfates.

The propene and butene which dissolved in the sulfuric acid in the form of sulfuric acid esters were determined by oxidation with sodium iodate, the excess of sodium iodate being determined by titration with sodium thiosulfate solution. From the volume of CH_2 determined by this analysis the index, or propene-butene ratio, was calculated, and from the volume per cent of propene plus butene, the volume per cent of each of these hydrocarbons in the original gas mixture was calculated.

After determining the proper conditions for oxidizing the sulfuric acid esters and determining the propene-butene ratio, the method was found convenient and accurate but time-consuming, approximately 2 hours being required for an analysis.

The method described here, in which the propene-butene ratio is obtained from the density of the mixture of propene and butene, was developed as an exceedingly rapid, routine procedure. It has been in use several months for the routine analysis of cracked refinery gases with entirely satisfactory results.

The determination of propene and butene by the molecular weight method consists primarily of two molecular weight determinations, one on the original gas, dry and free of carbon dioxide and hydrogen sulfide, and a second after the removal of propene and butene, the molecular weights being determined by means of a Stock electromagnetic gas balance. From the change in the molecular weight of the gas on the removal of the propene and butene by 87 per cent sulfuric acid and the volume per cent of propene and butene removed, the molecular weight of these olefins is calculated, and from this molecular weight the volume per cent of propene and of butene in the original mixture is calculated.

Ethylene is determined by absorption in concentrated sulfuric acid activated with nickel and silver sulfates. The activated acid is a mixture, in the proportion 1 to 15, of concentrated sulfuric acid (specific gravity 1.84) saturated with nickel sulfate at room temperature, and concentrated sulfuric acid containing 0.6 per cent of silver sulfate.

Ethylene is not appreciably dissolved by 87 per cent sulfuric acid if present in the gas mixture in concentrations of not over 20 per cent. If present in concentrations greater than this, the gas is diluted with air before making the absorption, so that it will not be necessary to make corrections for the ethylene absorbed.

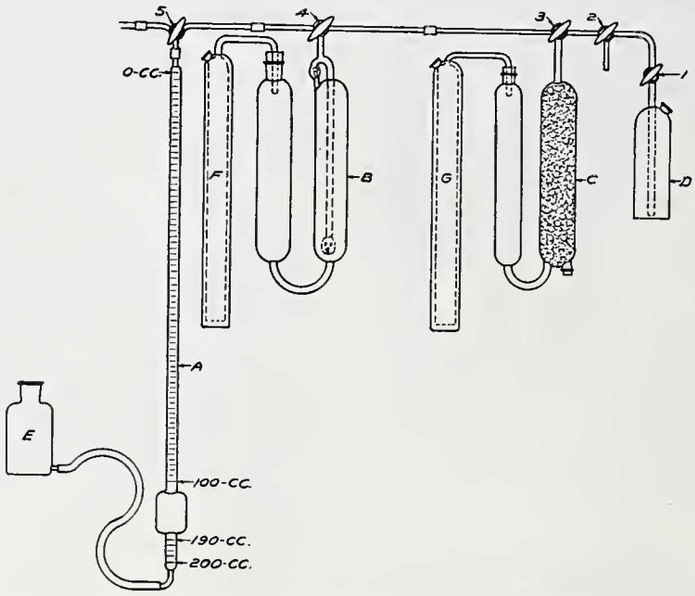

FIGURE 1. APPARATUS FOR DETERMINING PROPENE AND BUTENE IN GASES

[For drying tube, precision manometer, and magnetic gas balance, see Figure 2 (*2*)].

Apparatus

The apparatus, assembled as shown in Figure 1, consists of an absorption apparatus in connection with a magnetic gas balance. The buret, *A*, has a capacity of 200 cc. and is graduated in 0.1 cc. It is in connection with the absorption apparatus and the gas balance through the Karlsruhe stopcock, 5. The auto-bubbler, *B*, contains 33 per cent potassium hydroxide for the removal of carbon dioxide and hydrogen sulfide. Pipet *C*, filled with 6-mm. glass beads, contains 87 per cent sulfuric acid for the absorption of propene and butene. Two other pipets similar to *C*, containing 63 per cent sulfuric acid and activated sulfuric acid, are used for determining isobutene and ethylene.

The reservoir, *D*, and the leveling bottle, *E*, contain salt water, the solution in *D* being used for flushing the manifold through stopcocks 1, 2, 3, and 4. Traps *F* and *G*, containing the same solutions as the pipets, protect the solutions in the pipets from the atmosphere.

The drying tube (*2*, Figure 2) contains anhydrone for drying all gases that pass into the gas balance. The precision manometer and the magnetic gas balance have been described in an earlier paper (*2*).

Procedure

The calibration of the gas balance is made as previously outlined (*2*).

At the beginning of the analysis, all gas is removed from the buret and the manifold by displacement with salt solution. A sample of approximately 200 cc. is taken into buret *A* through stopcock 2, and passed into the potassium hydroxide solution to remove carbon dioxide and hydrogen sulfide. The volumes are recorded and approximately 100 cc. of the gas passed into the evacuated balance. The volume of the remaining gas is recorded and passed into pipet *C*, containing 87 per cent sulfuric acid, for 3 minutes. While this absorption is taking place, the molecular weight of the portion of the sample in the balance is determined. The milliammeter reading, the temperature of the balance, the manometer reading, and the temperature of the manometer are recorded. The balance is evacuated, and at the end of the 3-minute period the gas is passed from pipet *C* back into the buret for the volume reading, then into pipet *C* for a second 3-minute period if the first absorption shows an appreciable quantity of propene or butene. After the second absorption by 87 per cent acid, the gas is passed into the potassium hydroxide pipet, *B*, the manifold flushed with salt solution, and the volume recorded. The gas is then passed into the evacuated balance for the molecular weight determination of the propene- plus butene-free gas, recording the same data as for the first molecular weight determination.

The analysis requires about 10 to 15 minutes.

Calculations

The volume per cent of propene plus butene in the original sample is calculated from the volume absorbed by 87 per cent acid and the per cent of carbon dioxide and hydrogen sulfide removed by potassium hydroxide solution.

The apparent molecular weights, M, of the original and of the propene- plus butene-free gas, as read from the current molecular weight relation, are corrected to the molecular weight at 0° C. and 760 mm. pressure, M_1 and M_2, by means of the formula

$$M_1 \text{ or } M_2 = M \times \frac{760}{P} \times \frac{t + 273}{273} \qquad (1)$$

The following relations are used for calculating the volume per cent of propene and of butene in the original sample:

$$\text{Per cent } C_3H_6 = 4U + \frac{M_2 - M_1 - M_2U}{14.02} \qquad (2)$$

$$\text{Per cent } C_4H_8 = U - \text{per cent } C_3H_6 \qquad (3)$$

where M_1 = molecular weight of original gas
M_2 = molecular weight of gas after removal of propene and butene
U = volume per cent of propene plus butene in original sample

Analysis of Synthetic Mixtures

Representative analyses made of a synthetic mixture and the composition of the synthetic mixture are shown in Tables I and II.

Table I. Determination of Olefins by Molecular Weight Method

Determination	Volume Per Cent of Propene	Volume Per Cent of *n*-Butene
1	25.0	9.4
2	24.5	9.9
3	24.8	9.4
4	24.8	9.5
5	24.5	9.8
6	24.3	9.9
Av.	24.6	9.7
Calcd.	25.0	9.3

Table II. Composition of Synthetic Mixture

	%		%
Methane	53.8	Propene	25.0
Ethylene	11.9	*n*-Butene	9.3

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Determination of the Gasoline Content of Gases

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A low-temperature fractional condensation method for determining the gasoline content of gases has been developed and its application to the analysis of a wide variety of refinery gases has shown it to be suitable for the rapid, accurate, routine analysis of these gases.

A SUMMARY of the methods used previously for determining the gasoline content of gases has been given in an earlier review (*2*).

The method described here for the determination of the gasoline content of gases consists in condensing the hydrocarbons at the temperature of liquid nitrogen (−195° C.) and atmospheric pressure, removing methane and other difficultly condensable gases, especially dissolved nitrogen, under reduced pressure, and at low pressures fractionating the hydrocarbons in a U-tube cooled to −105° C., a temperature at which the hydrocarbons above C_4 are condensed. The hydrocarbons C_5 and higher are then vaporized into a known volume where the pressure and temperature can be measured. The gasoline vapors are condensed by liquid nitrogen in a bulb which is removed from the apparatus and accurately weighed. From the weight of the gasoline and the pressure it exerts when vaporized in a known volume at a definite temperature, the average molecular weight of the gasoline is calculated. From a curve relating the molecular weights to the specific gravities of the pure hydrocarbons, the specific gravity of the gasoline is read. With the weight of the gasoline from a known volume of gas and the specific gravity of the

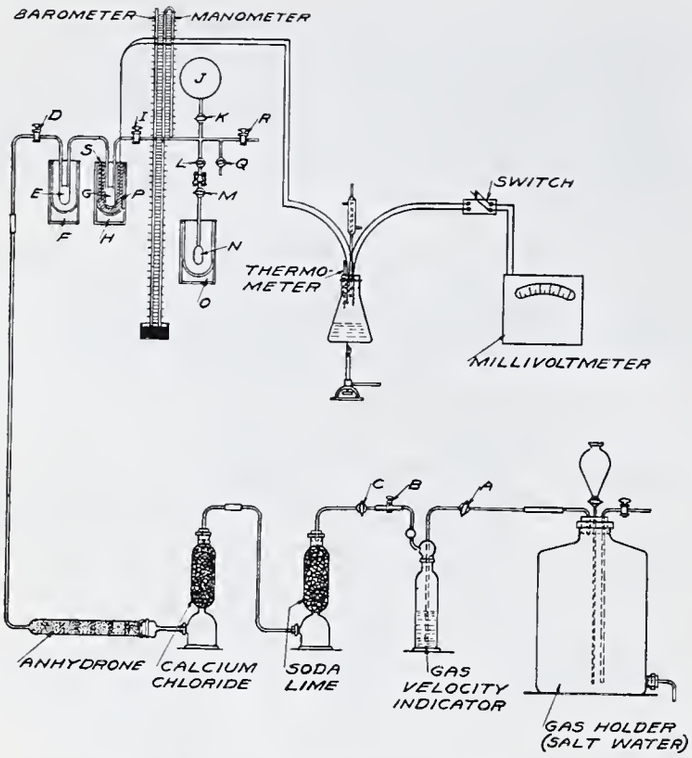

FIGURE 1. APPARATUS FOR DETERMINING GASOLINE CONTENT OF GASES

gasoline the gallons of gasoline per 1000 cubic feet of wet gas at 60° F. and 30 inches of mercury are calculated by substituting the values in a simple formula.

APPARATUS

The apparatus is shown diagrammatically in Figure 1.

A gas holder of 3- to 5-liter capacity containing saturated salt solution is used for measuring the gas sample. Absorption towers containing moist soda lime, calcium chloride, and anhydrone, or dehydrite, remove carbon dioxide and water vapor from the gases entering the condensation tubes. The Dewar flasks, *F* and *H*, are used as containers for liquid nitrogen to cool the U-tubes, *E* and *G*, during the condensation of the hydrocarbons. The aluminum block *P* (*1*, Figure 3), fitting inside Dewar flask *H* and around U-tube *G*, is provided with hole *S* for the introduction of the liquid nitrogen used to cool the block. An iron-constantan thermocouple is used for the temperature measurements. The junctions of the iron and the constantan wires with the copper lead wires from the millivoltmeter are maintained at a constant temperature of 100° C. by immersion in steam.

The volume of *J*, about 500 cc. (accurately determined), and the apparatus from *D* to *R* provide a volume sufficiently large for the complete vaporization of the gasoline fraction. The volume of the apparatus, including U-tubes *E* and *G* and bulbs *J* and *N*, is determined from the known volume of *J*. A connection is made at *R* to a vacuum pump which is capable of reducing the pressure in the apparatus to less than 0.001 mm. of mercury. A manometer connected directly to the apparatus is used to indicate the pressures. The weighing bulb, *N*, in connection with the apparatus through a ground-glass connection, is used to determine the weight of the gasoline fraction.

PROCEDURE

While the gas sample is being measured, the apparatus is evacuated through *R* until the mercury in the manometer tube stands at the same level as the barometer. The volume of the sample for the determination should be from 0.3 to 1 liter for gases containing more than 0.3 to 0.5 gallon of gasoline per thousand cubic feet (40 to 66 cc. per cubic meter) of gas, while for very lean gases (0.01 to 0.2 gallon of gasoline per 1000 cubic feet (1.3 to 26 cc. per cubic meter) as much as 1.5 to 3 liters is required. The sample volume is taken as the volume of the salt water displaced from the gas holder. The temperature of the sample is taken as the temperature of the salt water at the time the sample is measured. Pressure corrections are made for the vapor tension of the salt water and the decrease in pressure due to the height of the salt water above the lower outlet tube of the gas holder.

Stopcocks *K*, *L*, and *R* are closed and U-tubes *E* and *G* cooled by immersing in liquid nitrogen contained in Dewar flasks *F* and *H*. Screwclamp *B* is closed and stopcock *A* slowly opened to fill the gas velocity indicator (containing a small amount of mercury) with gas. After some experience in condensing the samples, the velocity indicator may be omitted and the rate judged from the pressure increase in the apparatus. The flow of gas into the condensation tubes is regulated by screwclamp *B* to a rate of about 100 cc. per minute. The pressure in the apparatus is gradually increased by methane and gases other than hydrocarbons which are not completely condensed, and if the pressure in the apparatus reaches atmospheric, stopcock *Q* is opened to allow these uncondensed gases to pass from the apparatus.

When the gas sample is displaced from the gas holder and the tubes to *A*, stopcocks *A* and *Q* are closed and the apparatus is slowly evacuated through *R*. If the evacuation takes place too rapidly, a part of the hydrocarbons is sometimes swept out of the U-tubes. While the uncondensed gases are being removed, the evacuated bulb *N* is removed and weighed to 0.1 mg., replaced on the apparatus, and *L* opened. When the pressure in the apparatus has been reduced to about 0.1 mm., *D* is closed and U-tube *E* allowed to warm slowly to distill the hydrocarbons into the second *U*-tube, *G*. Stopcock *I* is then closed and the hydrocarbons distilled back into *E*, removing through *R* any gases not condensed. These distillations are necessary to remove dissolved methane and nitrogen.

During these distillations, the aluminum block, *P*, is cooled to a temperature a few degrees below −105° C. The block is then placed around U-tube *G*, keeping the temperature at −105° C. by the occasional addition of small amounts of liquid nitrogen at *S*. Stopcock *I* is opened and the hydrocarbons in *E* are allowed to distill slowly at about 1 mm. pressure or less through *G* where the gasoline fraction is condensed. With gases containing appreciable quantities of butanes, a small amount of the C_4 hydrocarbons is condensed with the gasoline fraction but is completely removed by a second condensation. With all the hydrocarbons removed from *E* and the pressure reduced to less than 0.2 mm., *R* is closed, *K* and *M* are opened, and U-tube *G* is allowed to come to room temperature. The pressure of the vaporized gasoline, as indicated by the manometer, is recorded, together with the room temperature and the height of the mercury in the manometer tube.

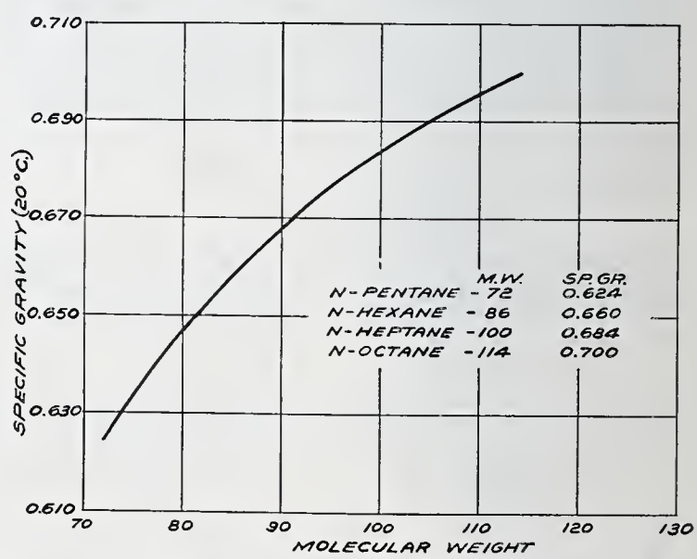

FIGURE 2. MOLECULAR WEIGHT–SPECIFIC GRAVITY CURVE FOR HYDROCARBONS C_5 TO C_8

Bulb *N* is then cooled in liquid nitrogen contained in the Dewar flask, *O*. The gasoline is condensed in *N* in a short time, as is indicated by the decrease in the pressure in the apparatus to 0.5 mm. or less. Small amounts of air in the apparatus make the complete condensation difficult, and for this reason air should not be admitted to bulb *J* or to other parts of the apparatus except when it is necessary to grease the stopcocks, etc. Stopcock *M* is closed and weighing bulb *N* removed and weighed to 0.1 mg. as soon as it reaches room temperature. The weight of the gasoline is obtained from this weight and the weight of the evacuated bulb.

The analysis requires about 30 to 45 minutes and approximately 150 to 200 cc. of liquid nitrogen.

Calculations

In this method the hydrocarbons C_5 and higher are determined as the gasoline constituents in grams per liter of dry gas at 0° C. and 760 mm. pressure. It is usually desirable to express the gasoline content in gallons per 1000 cubic feet of wet gas at 60° F. and 30 inches of mercury. To make this conversion, it is necessary to know the specific gravity of the gasoline. The average molecular weight of the gasoline is calculated from the weight of the gasoline and the pressure in a known volume at temperature t_2. Then from a curve, relating the molecular weights to the specific gravities of the pure hydrocarbons (Figure 2), the specific gravity of the gasoline is read.

The following relations have been derived by which the calculations are easily made:

$$M = \frac{22410 \times g \times 760(t_2 + 273)}{P_2(V_2 - \pi r^2 h)\ 273} \qquad (1)$$

$$G = \frac{19.39 \times g(t_1 + 273)}{S \times P_1 \times V_1} \qquad (2)$$

Where

M = average molecular weight of gasoline
G = gallons of gasoline per thousand cubic feet of wet gas at 60° F. and 30 inches of mercury
g = weight of gasoline, grams
S = specific gravity of gasoline at 20° C.
V_1 = volume of gas sample, liters
V_2 = volume of apparatus
P_1 = pressure of gas sample, mm.
P_2 = pressure of gasoline vapor, mm.
t_1 = temperature of gas sample, ° C.
t_2 = room temperature when gasoline fraction is vaporized, ° C.
h = height of mercury in manometer, cm.
r = radius of manometer tube, cm.

A nomograph, Figure 3, facilitates the reduction of gas volumes to standard conditions.

Accuracy of Method

The accuracy of the above method for determining specific gravity was checked by determinations on samples of commercial pentane, hexane, and heptane. The procedure was to introduce from 0.05 to 0.30 gram of the hydrocarbon into the apparatus, removing dissolved gases, making the molecular weight determination as outlined, and reading the specific gravity from the specific gravity–molecular weight curve, Figure 2. The data in Table I were obtained for a sample of pentane.

Table I. Specific Gravity of Pentane by Molecular Weight Relation

Sample No.	Pentane	Molecular Weight	Specific Gravity (from Curve)	Deviation from Mean Sp. Gr.
	Gram			
1	0.0554	71.8	0.624	−0.003
2	0.0736	73.1	0.627	0.000
3	0.0799	71.7	0.624	−0.003
4	0.1202	72.8	0.627	0.000
5	0.1215	72.9	0.627	0.000
6	0.1262	73.4	0.629	+0.002
7	0.1286	72.1	0.624	−0.003
8	0.1412	73.4	0.629	+0.002
9	0.1522	73.1	0.627	0.000
10	0.1574	72.0	0.624	−0.003
11	0.2776	72.6	0.626	−0.001
12	0.2785	73.4	0.629	+0.002
13	0.2806	73.2	0.627	0.000
14	0.2837	72.7	0.626	−0.001
15	0.2903	72.8	0.627	0.000
16	0.2980	72.5	0.626	−0.001
17	0.3077	73.3	0.629	+0.002
	Mean sp. gr.		0.6265	
	Mean deviation from av.		0.0013	
	Sp. gr. by Westphal balance		0.626	

The results of similar determinations on hexane and heptane are summarized in Table II.

Table II. Specific Gravity of Hexane and Heptane by Molecular Weight Relation

Sample No.	Hydrocarbon	Specific Gravity From curve	Specific Gravity By Westphal balance
1	Hexane	0.671	0.662
2	Hexane	0.660	0.662
3	Hexane	0.666	0.662
4	Hexane	0.664	0.662
5	Heptane	0.687	0.684

The analysis of synthetic mixtures of nitrogen, butane, and pentane containing approximately 5 per cent of butane and 3 per cent of pentane has served as a further check on the accuracy of the method. The calculated values are compared with the experimental values in Table III.

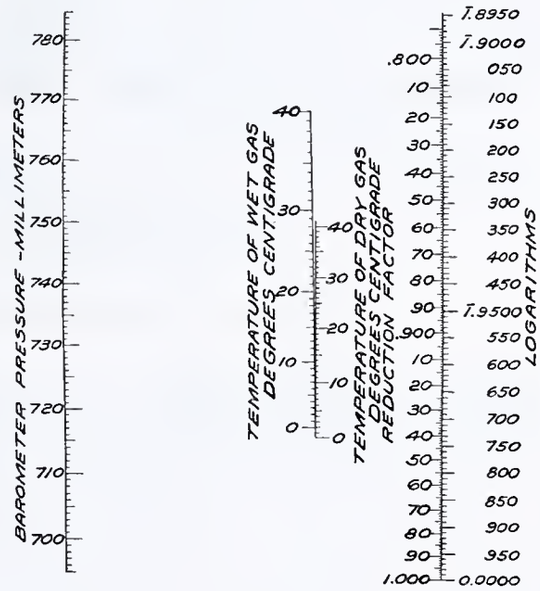

Figure 3. Gas Reduction Chart

Table III. Determination of Pentane in Synthetic Nitrogen-Butane-Pentane Mixtures

Sample No.	Pentane Calculated	Pentane Found
	Gal./1000 cu. ft.	*Gal./1000 cu. ft.*
1	1.02	1.02
2	1.08	1.07
3	1.09	1.06
4	1.15	1.15

Analyses made on plant refinery gases by the low-temperature condensation method are compared, in Table IV, with analyses made on the same samples by the Podbielniak method.

Table IV. Analysis of Refinery Gases. Comparison with Podbielniak Method

Sample No.	Method: Fractional condensation	Method: Podbielniak
	Gal./1000 cu. ft.	*Gal./1000 cu. ft.*
1	0.0	0.0
2	0.45	0.76
2	0.46	..
3	0.54	0.36
4	1.43	1.45
5	3.16	3.17

This method gives results in good agreement with those of the Podbielniak apparatus on gases of high gasoline content, approximately 2 gallons per 1000 cubic feet or over. With gases of low gasoline content, particularly if nitrogen is present, it is much more reliable than the Podbielniak apparatus. Gases which could not be analyzed by the Podbielniak method on account of the high nitrogen content, over 70 per cent, have been analyzed satisfactorily and without difficulty by the fractional condensation method.

The method has been applied in the analysis of a large number of refinery gases. Typical examples are given in Table V.

Table V. Analysis of Gases Entering and Leaving an Absorption Plant

(Gallons of gasoline per 1000 cubic feet of gas)

Sample No.	Gas Entering Absorption Tower	Exhaust Gas	Approximate Recovery
1	0.26	0.08	0.2
2	0.34	0.16	0.2
2	0.35	0.16	0.2
3	0.43	0.12	0.3
4	0.92	0.21	0.7

Samples were taken of the plant gases entering the absorption system and also of the exhaust gases leaving the plant. The difference between the gasoline content of the exhaust gases and that of the gases entering the absorption system was in close agreement with the quantity of gasoline collected from the absorption.

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Determination of Tie Lines in Ternary Systems

Without Analyses for the Components

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Ternary liquid systems are generally characterized by plotting on a triangular field the curves separating the regions of homogeneity and heterogeneity, together with the tie lines connecting the points representing conjugate phases. The boundary curves may usually be easily obtained by titrating a homogeneous mixture of two of the components with the third until turbidity appears, thereby securing one point. To determine the tie lines, however, no simple method, except that of Miller and McPherson (*1*), seems to have been developed that does not require a direct analysis for at least one of the components (*2*). Inasmuch as systems are often investigated in which none of the components can be accurately or easily determined it is desirable to have some rapid method of determining the tie lines which is independent of chemical analyses. The following method seems new, is applicable in the usual cases, and compares favorably with that of Miller and McPherson in ease of manipulation.

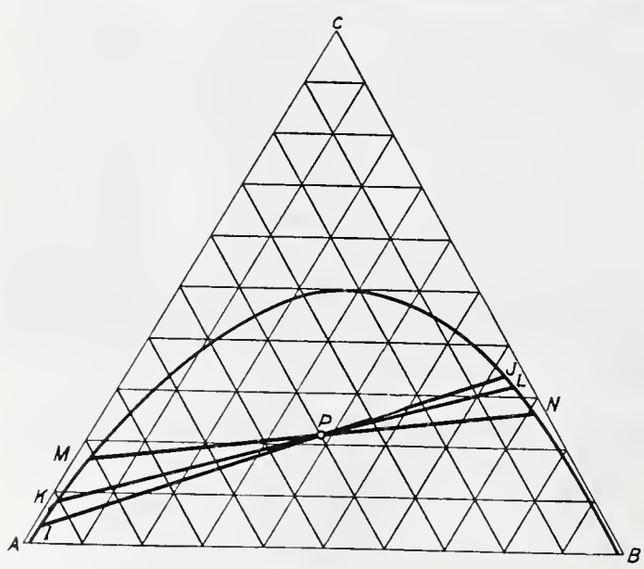

Figure 1

In Figure 1 is shown a typical ternary diagram for the system of three components A, B, and C. Suppose weighed amounts of the three components are now taken in such amounts that the over-all composition is represented by the point P. This mixture upon shaking and settling will give two layers, the composition of the lower layer being represented by a point on, say, the left-hand portion of the curve, the upper layer on the right-hand side. The line joining these two points is a tie line and passes through P. Through P draw the lines IPJ, KPL, and MPN. Ordinarily the composition of lower and upper layers can be estimated roughly and the lines drawn so that these compositions lie somewhere between I and M, and J and N. Assume this is the case here; in case it is not, the discrepancy will appear later and if necessary one of the lines can be changed accordingly. Let m_1, m_2 be the weights of the upper and lower layers obtained, m_A, etc., the weights of the components taken, and L_A, etc., the percentage of component A corresponding to the point L.

In case KPL is the true tie line we have $0.01(m_1L_B + m_2K_B) = m_B$. In general KPL will not have been so chosen as to be the exact line, and hence $0.01(m_1L_B + m_2K_B)$ will not equal m_B. However, by plotting the value of this expression for the three lines drawn against the percentage B of the points on the right-hand branch of the curve or the percentage A on the left branch, a value of these percentages will be obtained for which the expression does equal m_B. By now locating this point on the curve and joining it to P the tie line is secured. In the same way the percentage A could have been used. The essential point to the process is that as we proceed from I to M the percentage B does not change greatly, and what change there is is in a positive direction, while from J to N the change is very rapid and positive, thus making the method relatively sensitive. It is evident that the C component would not be suitable, since it increases from I to M and decreases about equally from J to N, the two effects offsetting each other and rendering the variation in $0.01(m_1L_C + m_2K_C)$ too small to be useful. The following example will illustrate the method.

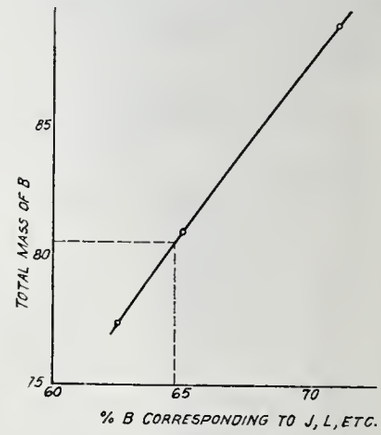

Figure 2

A mixture of 84.5 grams of A, 80.5 grams of B, and 46.5 grams of C is shaken and on settling is found to give 122.5 grams of upper layer and 89.0 grams of lower layer. Point P in Figure 1 represents this over-all composition—namely 40, 38, and 22 per cent.

Now if IPJ were the true tie line, the mass of B should be $0.01[(89.0)(1) + (122.5)(62.5)] = 77.4$ grams. Similarly KPL demands 80.9 grams and MPN 89.0 grams, whereas the true line should give the amount of B originally taken, 80.5 grams. By plotting these values against the percentage B represented by the points J, L, and N, the percentage corresponding to a value of 80.5 is found to be 64.7 (Figure 2). This percentage when located on the curve of Figure 1 indicates that the upper layer obtained above is 3 per cent A, 64.7 per cent B, and 32.3 per cent C. By joining this point to P the tie line is obtained. As a check on the work, the above process can be repeated on component A, this time locating a point on the left side of the curve which when joined to P gives the tie line. If both times the same tie line is obtained, one can feel sure of the accuracy of the work. In the present case the percentage A is found to be 91, thus locating the point on the curve 91 per cent A, 1.5 per cent B, 7.5 per cent C. This also lies on the tie line secured by computing on the basis of component B, thus checking the previous work. Finally, using the values so obtained for the percentage C in each layer, it is found that on this basis we should have started with $0.01[(89.0)(7.5) + (122.5)(32.3)] = 46.3$ grams of component C, which is in satisfactory agreement with the 46.5 grams actually taken.

In the present case the auxiliary lines IJ, etc., were so drawn that they lay on either side of the tie line. In case they had been so chosen that they all lay on the same side of the tie line, this fact would have instantly appeared on graphing the expression $0.01(m_1J_B + m_2I_B)$, since it would have been greater (or less) than m_B for all the lines instead of greater for one and less for another. In many cases the graph could still be successfully extrapolated. If the extrapolation seemed uncertain, then another line could be chosen so as certainly to lie beyond the tie line, and by adding this value to the graph the required value easily determined by interpolation.

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Chemical Studies of Wood Preservation

III. Analysis of Preserved Timber

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Methods are given for analysis of preserved timber, whether creosoted or treated with inorganic salts. The methods are in part adapted for appraisal of freshly treated poles for quantity and excellence of distribution of preservative and in part adapted to following the processes of depletion during years of exposure. Recovery of creosote from old timber and methods for the analysis and toximetry of creosote are described.

In the study of the preservation of poles, one may distinguish several kinds of samples for chemical analysis classified according to the purpose of the study:

1. Samples of freshly treated timber taken for the purpose of determining the quantity of a known preservative and the character of its distribution.
2. Samples from poles still required for service or further exposure in experimental plots. These samples may be used to determine roughly the changes in quantity, distribution, and toxicity of preservatives with time.
3. Samples of poles which have been removed from service lines or from experimental plots and are therefore available for more thorough study of the changes in properties of preservatives with the lapse of years.

It is the purpose of the present paper to outline the analytical methods used for the examination of the foregoing classes of samples. While these studies are primarily concerned with creosote, the authors have examined many other preservatives more or less thoroughly. For this purpose it has been necessary to devise special analytical methods in certain cases.

Analysis of Freshly Treated Timber

The purpose of an examination of freshly treated timber is usually to secure some measure of the excellence of a treating process at a particular plant or by a particular method. In this case a sample of the original preservative is available for thorough examination of its physical and chemical properties as well as toxicity. Since it is unnecessary to recover the preservative from the samples in its original state, one has a freer choice of analytical methods. It is often highly desirable that the method of analysis of wood be rapid and inexpensive in order to permit the examination of a substantial proportion of all the poles and the delivery of the results of analysis within a few hours.

In order to determine the penetration and retent of the individual poles in any particular charge, it would be necessary to take several borings around the circumference of each pole and perform an analysis on the composite borings from each pole separately. Except for very special purposes this is too laborious. A single boring from each pole will suffice to give a fairly good appraisal, provided each boring is examined for depth of sapwood and depth of penetration as well as preservative content. A great deal can be learned by sampling only a selected proportion of the poles. The borings may be split for analysis as described in a previous paper (*9*), though for some purposes the whole boring may be analyzed and an empirical correction or an arbitrary standard of preservative content may be applied.

In the case of freshly creosoted poles the following method of determining creosote has been found convenient:

The heartwood and untreated sapwood are broken off the borings, and the samples thus obtained are chipped up and placed in a tared brass container provided with a screen bottom and weighed. This container is then placed in the apparatus shown in Figure 1. The solvent, which may be either toluene or xylene, is boiled, and as the vapors extract the wood, the water is carried up into the condenser and drops into the calibrated trap. The extraction is continued until the solvent dripping from the cage is colorless and water ceases to drop into the trap. The solvent is evaporated from the extracted wood, which is then brought to constant weight at approximately 105° C. The water content is read directly in the trap. The weight of water plus the dry weight of wood subtracted from the original weight

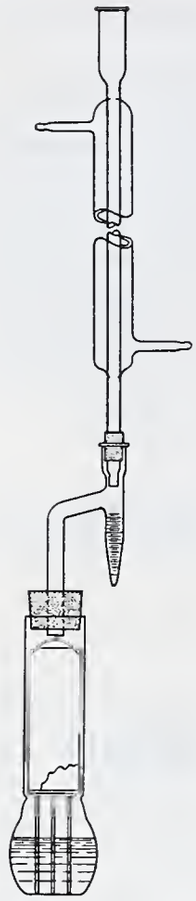

Figure 1. Apparatus for Determining Creosote

gives the creosote content. Using the weight of creosote thus found, the retent per unit volume is calculated from the diameter of the boring, the radius of the pole, and the number of borings taken.

This method involves ignoring the weight of natural extractives derived from the wood. Air-dried untreated sapwood of several samples of southern pine has been extracted and never found to contain more than 0.2 pound per cubic foot (0.32 gram per 100 cc.) of toluene- or xylene-soluble material such as resins. The amount is usually even less and has therefore been neglected in all this work. Care must be taken in sampling poles which have been felled only 2 or 3 days before treatment. Such wood may still contain very volatile compounds such as terpenes which may lead to falsely high results for creosote content. Steam conditioning lessens the chance for this error, but it is well after splitting the borings to leave them in the open for a few minutes before weighing in the case of poles which were treated when extremely green. Creosote losses from the exposed borings are small, as they cool rapidly.

In order to indicate experimentally the accuracy of the toluene extraction method, a weighed amount of creosote was added to a given weight of sawdust in a tared metal extraction thimble and extracted as described above with the results recorded in Table I.

An adaptation of this method of retent determination has been in use for some time in the Bell System for creosoted Douglas fir poles. The chips from an ordinary wood bit are used for analysis and an arbitrary standard of creosote content is chosen.

Aside from the creosote content, the depth of penetration in relation to the depth of sapwood is a very important index of efficiency of impregnation. It is well to record these figures for statistical examination. When the line of demarcation between the sapwood and heartwood is not clearly evident in the case of southern pine, use is made of a staining test. The test is performed as follows:

The boring as it comes from the increment borer is often smeared with oil. It is therefore split longitudinally to provide a clean surface. The edge of the face of the split boring is brought in contact with the surface of a water solution of nigrosine black or cotton blue, so that the rate of absorption as well as intensity of the discoloration of the wood can be readily observed. As a rule the dye solution is absorbed readily by the sapwood, but not by the heartwood. Any dark dye which is not actually adsorbed by the wood and hence taken out of solution would probably be satisfactory. Experience is necessary in interpreting the results when abnormal or irregular conditions are encountered.

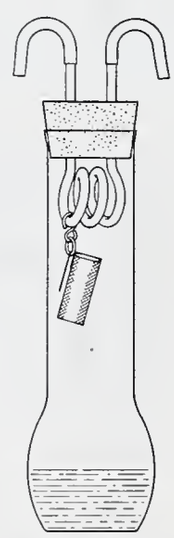

Figure 2. Apparatus for Indirect Determination of Creosote

Table I. Toluene Extraction of Creosote

No.	Sawdust	Creosote Added	Creosote Found	Error
	Grams	*Grams*	*Grams*	%
1	55.675	10.379	10.596	+2.09
2	55.705	11.538	11.499	−0.34
3	55.487	10.876	11.117	+2.22
4	54.234	11.593	11.547	−0.40
5	46.671[a]	10.483	10.138	−3.29
6	45.413[a]	10.795	10.235	−5.19
7	55.607[a]	11.968	11.213	−6.31

[a] Sawdust equilibrated over water prior to addition of creosote.

Analysis of Samples from Standing Poles

When examining creosoted poles which have been exposed for some months or years, it is desirable to use a nontoxic solvent, so that the toxicity of the extract can be determined as well as the retent in the pole at the time of sampling. This excludes the use of benzene, toluene, etc., as extractants, as the low-boiling cyclic hydrocarbons in general are extremely toxic and difficult to remove completely from creosote. Ether is preferred on account of its low toxicity, but it also is so difficult to remove completely that the determination of amount of creosote is best made indirectly.

The borings from the test poles, usually eight per pole, taken from the region of special interest, are split diagonally and the heartwood and untreated sapwood discarded. The rest is cut up into small pieces, placed in a small tared wire basket, and put over calcium chloride until at constant weight. This requires from 2 to 4 weeks. Usually scores of these determinations are run in parallel, so that the time required is not serious. The basket is then suspended from a water-cooled condenser in a tall form flask over boiling ether (Figure 2). The extraction is continued until the drip from the basket is colorless. The basket is then removed, and after the ether has evaporated is replaced over calcium chloride until again at constant weight. The difference in weight before and after extraction thus represents the extractive. The step of bringing the wood back to equilibrium over calcium chloride a second time may be dispensed with by merely drying in an oven at 105° C. and applying a suitable correction factor based on the moisture content of the wood in equilibrium with calcium chloride. This has been found from experience to average 1.39 per cent, dry weight basis, for southern pine sapwood. The ether extract obtained in this process is reserved for tests of its toxicity by methods referred to below.

The accuracy of the ether extraction method is indicated by experiments involving the addition of a weighed amount of creosote to an appropriate weight of sawdust and subjecting the samples to extraction (Table II).

Table II. Ether Extraction of Creosote

No.	Sawdust	Creosote Added	Creosote Found	Error
	Grams	*Grams*	*Grams*	%
1	8.267	2.193	2.091	−4.65
2	8.890	2.146	2.090	−2.47
3	8.600	2.164	2.114	−2.31
4	8.136	2.072	1.947	−6.03
5	7.324[a]	2.269	2.261	−0.35
6	7.446[a]	2.172	2.163	−0.41
7	8.162[a]	2.317	2.258	−2.55
8	7.456[a]	2.026	2.002	−1.18

[a] Samples equilibrated over water prior to addition of creosote.

Analysis of Discarded Poles

During the past few years scores of creosoted poles which presented some feature of special interest, such as early failure or outstandingly good performance, have been available for examination. In addition many pole sections have been removed from test plots for dissection and analysis. In such cases a more liberal sampling is possible, as there is no necessity for keeping the pole intact for further exposure or observation. Such examinations are for the purpose of qualitative information regarding the kind of changes which have occurred. Quantitatively, they are often of limited value on

account of uncertainty as to the representative character of the pole chosen for examination.

The procedure is to cut a cross-sectional slab about 1 inch (2.5 cm.) thick from the above-ground portion of the pole and another from below ground for determination of sapwood depth, depth of penetration, and amount of creosote still present. The slabs are cut into several sectors as nearly as possible representative of the entire cross section and the average sapwood and penetration are measured. The wedge-shaped pieces may be divided into an outer and inner treated part, an untreated sapwood portion when present, and the heartwood. The volume of each section is measured by mercury displacement in a graduated cylinder. When it is desired to determine only the quantity of oil present, the selected treated parts are cut up into slices approximately 1 inch wide by 0.063 inch (2.5 × 0.16 cm.) thick and extracted with toluene or xylene as outlined under "analysis of freshly treated timber." Calculations are made of creosote content of the entire sector or of the different parts of the cross section, according to the information desired.

In order to get some indication of the type of oil originally present and to find how it has changed through the years, several cross-sectional slabs cut from the pole both above and below ground are separated into an outer and inner treated section; the wood is sawed and split into pieces roughly 0.75 × 0.75 × 2 inches (1.9 × 1.9 × 5 cm.), and put through a hog to reduce it to sawdust. The sawdust, usually 2 to 10 lbs. (1 to 5 kg.), depending on the operator's judgment of the oil content, is placed in the extractor shown in Figure 3. The sawdust is contained in the false bottom cage which is 15 inches (37.5 cm.) high and 11.5 inches (28.75 cm.) in diameter and ether is poured in from the top. The ether is boiled by circulation of water at 45° C. and is condensed by the water-cooled coils attached to the hinged cover. Flexible hose is used to connect the cold water supply with the condenser. During the extraction the cock on the side

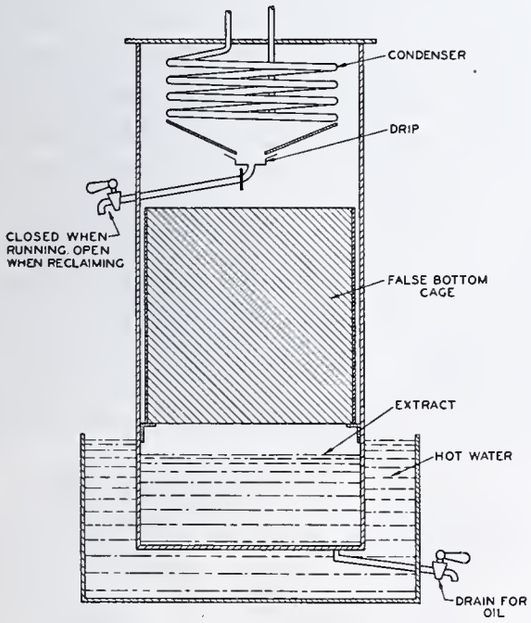

FIGURE 3. EXTRACTOR

is closed, allowing the ether to drip down through the sawdust. When extraction is complete, usually in less than 2 days, this cock is opened to reclaim the ether. The residual oil after being further freed of ether by gradually bringing to steam bath temperature is available for analysis as in the case of new creosote.

A battery of four such extractors is illustrated in Figure 4. They are operated in a small room separated from all other laboratory operations and provided with vigorous ventilation and safety devices on electrical outlets.

METHODS OF GENERAL APPLICATION

TOXIMETRY. The toxic potency of preservatives has usually been determined in essentially the same manner as at the Forest Products Laboratory, Madison, Wis. (*7*).

Samples of the substances under test (usually ethereal solutions in the case of creosote) are weighed or measured and introduced into a hot mixture of malt, agar-agar, and water in glass-stoppered bottles. The bottles are shaken vigorously and the agar is poured into Petri dishes, or the whole operation may be carried out in glass-stoppered Erlenmeyer flasks or preferably Petroff

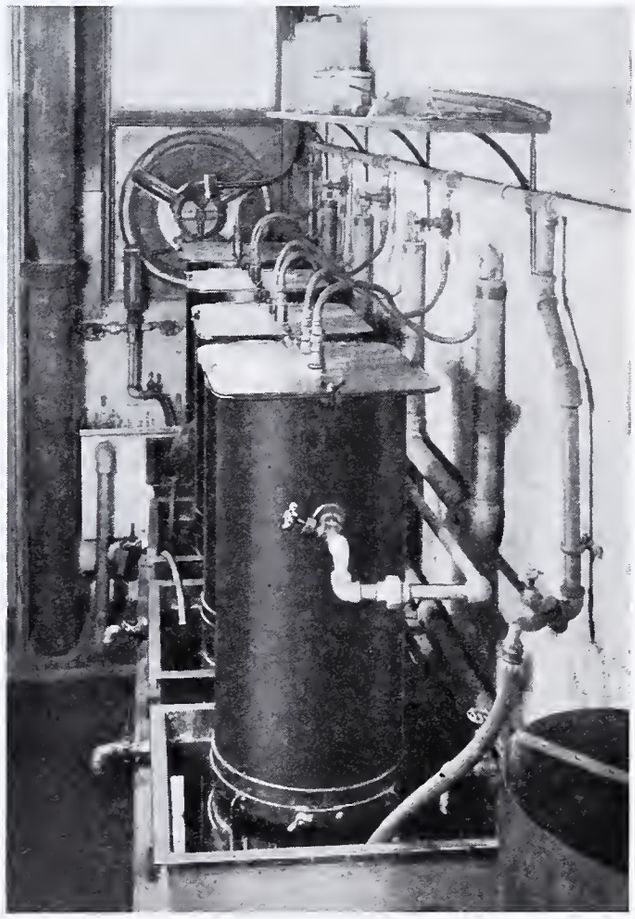

FIGURE 4. BATTERY OF FOUR EXTRACTORS

flasks sealed with gelatin bottle caps. After the agar cools and gels, the medium is inoculated with a pure culture of a wood-destroying fungus. If no growth has taken place after an incubation period of 4 weeks, the inoculum is removed and placed on nontoxic agar to determine whether it has been killed or merely inhibited by the action of the toxic substance.

At present the fungi most in use in this laboratory are *Fomes annosus*, *Lentinus lepideus*, *Poria incrassata*, and *Coniophora cerebella*, all obtained originally through the courtesy of the Forest Products Laboratory.

A more extended discussion of various toximetric methods, results, and interpretations will appear in a later paper.

CREOSOTE ANALYSIS

Whenever possible the methods of the American Wood Preservers' Association (*1*) are followed in creosote analysis. The manual of the association does not include a method for sulfonation residue. For this purpose 37 *N* sulfuric acid is used as the sulfonating agent and the unsulfonated residue is read after centrifugalizing in Babcock milk-test bottles. The authors prefer for the sake of expedition to determine tar acids by extracting the oil in benzene solution with sodium hydroxide, followed by liberation of the acids from the aqueous solution with sulfuric acid, rather than to use the American Wood Preservers' Association method.

A rapid method for determination of water in creosote is sometimes needed. For example, in the empty cell treatment

of green wood, some water accumulates in the creosote. To facilitate control of this feature, the following method was developed:

The apparatus as shown in Figure 5 is similar to that used in water-content determinations for various organic compounds utilizing a solvent lighter than water, but with a higher boiling point. Toluene, xylene, or naphtha are boiled vigorously in the apparatus; when no further traces of water appear at the end of the condenser, the stopcock on the trap is opened momentarily to remove any traces of water which may have collected. The creosote is added slowly through the separatory funnel and after a few minutes' boiling all water present has passed into the graduated trap and the quantity is read directly. This water can be drained out of the trap, and the apparatus is ready for another determination without recharging with toluene.

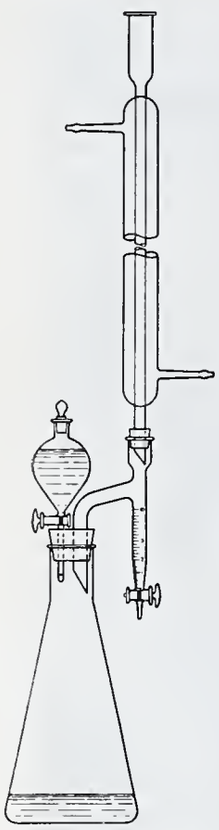

Figure 5. Apparatus for Determining Water in Creosote

Analysis of Wood Preserved with Inorganic Materials

For the purpose of destroying organic matter to permit determination of metal ions in wood, the authors have found the method of Bateman (*2*) very useful. This consists in digesting a known volume or weight of wood with a saturated solution of potassium chlorate in concentrated nitric acid, adding sulfuric acid, and boiling down to fumes, with repeated additions of a few drops of concentrated nitric acid if necessary to destroy the last traces of organic matter. This method has the advantage over leaching of insuring the complete recovery of all metal ions. In some instances, there is reason to suspect that certain metal ions become fixed in the wood in such a way as to become inoperative in a preservative sense. This is notably true of certain copper, zinc, and chromium preparations. When this is suspected a leaching method may be used for determining the "available" metal ion in which case the organic matter in the evaporated extract may be destroyed in the manner above described. The matter of determination of effective metal ions present as distinguished from the total metal ions has not yet been thoroughly studied.

Arsenic. Determination of small amounts of arsenic is made by the Sanger Black method (*8*) with slight modifications upon an aliquot of the solution prepared according to Bateman.

Determination of large amounts of arsenic is made by distillation of a solution of 5 grams of wood prepared in the same manner. For this purpose the digestion flask is attached to a thistle tube and connected to a condenser after addition of 2 grams of hydrazine sulfate and 5 grams of potassium bromide to reduce the arsenic to the arsenous form. Sixty to 70 cc. of concentrated hydrochloric acid are added through the thistle tube and distillation is carried on until the volume is reduced to 15 to 20 cc.; hydrochloric acid is again added and distillation repeated as before. This is continued until the final distillates are free from arsenic, as shown by a test with hydrogen sulfide. Distilling off two portions of acid is usually sufficient. The combined distillates are neutralized with ammonia, treated with 5 grams of sodium bicarbonate, and titrated with 0.1 *N* iodine using starch as indicator. A blank correction is made.

The precision of this method may be judged from analyses which were made of mixtures of sawdust and arsenic trioxide in known proportions (Table III).

Table III. Determination of Arsenic

Sample: Arsenic trioxide	Sample: Wood	Arsenic Trioxide Found
Gram	*Grams*	*Gram*
0.0502	3.0	0.0486
0.0502	3.0	0.0483
0.0251	3.0	0.0241
0.0251	3.0	0.0241
0.0100	3.0	0.0095
0.0100	3.0	0.0095

Zinc in Presence of Arsenic. Determination of zinc in the presence of arsenic is performed upon the residue from the arsenic distillation. Iron is usually present in appreciable amounts and must be removed. This is done by oxidizing with ammonium persulfate, adding ammonium chloride and ammonia, and filtering off the ferric hydroxide. The solution is then evaporated to dryness and brought down to fumes with sulfuric acid. The resulting solution is titrated with potassium ferrocyanide using diphenylamine as indicator to an apple green end point (*3*). This titration is also applicable to the determination of substantial amounts of zinc when present as residues from zinc chloride treatments—that is, in the absence of arsenic. If only minute amounts of zinc are present, an aliquot of the solution after destruction of organic matter is freed of iron and precipitated in a Nessler tube with potassium ferrocyanide. The final determination is made nephelometrically.

Copper in Presence of Zinc. Copper is determined in the presence of zinc by precipitation as copper sulfide after destruction of organic matter. The filtrate from the copper sulfide is used for the zinc determination as above. The copper sulfide is dissolved in a solution of bromine in hydrochloric acid, brought down to fumes with sulfuric acid, and copper is determined colorimetrically as the ferrocyanide.

Mercury. Determination of mercury in wood subjected to mercuric chloride treatments has been the source of some difficulty. It was found that some mercury is volatilized if organic matter is destroyed by Bateman's method. Accordingly, a sample of the wood is reduced to sawdust by means of a rasp and a weighed amount (5 to 10 grams) is suspended in 150 cc. of water and 50 cc. of concentrated nitric acid in which is dissolved 1 gram of potassium permanganate to maintain an oxidizing condition in the solution. The suspension is then electrolyzed for 2 hours with a current of 1 ampere, using a rotating platinum electrode. The cathode is raised from the solution and washed with distilled water before interrupting the current. The mercury is now dissolved with about 30 cc. of concentrated nitric acid at 45° to 50° C. The electrode is washed in water and the solution is diluted to 100 to 125 cc., filtering if necessary to remove any particles of sawdust which have adhered to the electrode. The mercury is oxidized with a slight excess of potassium permanganate solution and any excess permanganate is quantitatively removed by addition of dilute hydrogen peroxide. Ferric sulfate is added as indicator and the solution is titrated with 0.01 *N* ammonium thiocyanate. In order to insure that no mercury has been left in the original sawdust residue the electrolysis should be repeated in case of uncertainty and any additional mercury obtained is oxidized and titrated as before.

Table IV. Determination of Mercury

Sample: Mercuric chloride	Sample: Wood	Mercuric Chloride Found
Gram	*Grams*	*Gram*
0.0050	3.0	0.0049
0.0100	3.0	0.0099
0.0100	3.0	0.0093
0.0050	3.0	0.0047

Borax. Determination of borax is made by a modification of the Thompson method (*5*). The wood is first extracted with hot water in a Soxhlet-type extractor, concentrated to a small volume, and the Thompson method followed except that mannitol is used in place of glycerol in the titration.

Fluorine. Determination of fluorine in wood treated with sodium fluoride alone presents no especial difficulties. The finely divided sample is ignited in a platinum crucible; the ash is dissolved in hot water and any insoluble material filtered off. From this point on, the lead chlorofluoride method outlined by Hawley (*4*) is followed.

Determination of fluorine in the presence of arsenic or chromium or both requires special methods. The method outlined below gives approximate results.

The chipped sample in a crucible is moistened with sodium hydroxide and sodium carbonate solution, dried, and ignited at 800° C. (± 50°) until all organic matter has been destroyed. The residue is dissolved in hot water and filtered; the solution is cleared of chromium and arsenic with excess silver nitrate. The

excess silver is removed with sodium chloride and the fluorine in the filtrate is determined as follows (*6*): Ammonium hydroxide is added in excess and the solution boiled down to 40–50 cc. A 7.0-cm. ashless filter paper is added and thoroughly macerated and 10 cc. of 2 *N* calcium nitrate are added to the hot solution to precipitate the fluorine. The solution is cooled, filtered, and washed (filtrate and washing should not exceed 100 cc.). The residue is ashed in a platinum crucible and weighed as calcium fluoride.

Data on the accuracy of such fluorine determinations are given in Table V.

Table V. Determination of Fluorine

Sample		Sodium Fluoride Found
Sodium fluoride	Wood	
Gram	*Grams*	*Gram*
0.0125	3.8	0.0110
0.0153	5.0	0.0114
0.0216	5.0	0.0183

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IV. Small Sapling Method of Evaluating Wood Preservatives

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In order to expedite tests of the permanency of pole preservatives, use is made of groups of small pine saplings treated with the preservative in question and set in the ground as miniature telephone poles. In these specimens weathering is relatively rapid on account of the large ratio of surface to volume, and poorly preserved material begins to decay in 1 or 2 years. Analyses and toxicity tests as well as observations of decay are made periodically. Seven years' experience indicates that the comparative preservative values of various salts, creosotes, oils, etc., may be estimated relatively cheaply, quickly, and with considerable reliability by this method.

Permanence and toxicity are probably the most necessary characteristics of a wood preservative. Ease of injection, freedom from corrosive properties, cleanliness, cost, and the like are all important, but no material can be considered unless it displays a high degree of resistance to wood-destroying fungi and unless this toxic potency persists when the treated wood is exposed to the weather for long periods of time. The problem under discussion is that of appraisal of wood preservatives for these two characteristics within a reasonably short time.

Methods are gradually becoming standardized for toximetric determinations and if this were the sole consideration, judging preservatives would be greatly simplified. However, permanence is equally important and is more difficult to estimate. It may be measured to a degree by laboratory determination of the evaporation and leaching rates of oils and salts, respectively, but a true measure of the utility of a preservative should include something closely resembling outdoor exposure and a measurement of the rate of decline in amount and potency of the preservative. Preferably these observations should be extended till actual rotting occurs, at least in the case of less satisfactory products. In dealing with such a complicated chemical, physical, and biological process, laboratory tests have definite handicaps and it is always possible that some vital factor has been missed. A complete life observation within a short time is the end to be desired and the use of small specimens exposed to a warm moist climate permits an approach to this ideal.

The method chosen makes use of small saplings of southern yellow pine about 0.5 inch (1.27 cm.) to 0.75 inch (1.94 cm.) in diameter and 30 inches (76.2 cm.) long. The ratio of surface to volume, expressed in inches, in the average pole in use in the Bell System is approximately 0.467. In a sapling of 0.75 inch (1.94 cm.) diameter this ratio is 5.33. Hence for a given unit of volume the sapling has a surface available for evaporation or leaching 11.42 times as large as the average pole with a diameter of 8.56 inches (21.7 cm.) and accordingly tends to rot much sooner. (The treated volume of wood in a pole is normally somewhat smaller than the total volume, thus reducing the effective ratio perhaps to 9 or 10. However, other factors, notably longitudinal diffusion from below ground upward, further complicate the comparison and prohibit an exact treatment of it.) The saplings are easy to obtain, and are better than turned sticks in that they approximate a pole in which the grain runs parallel to the surface. The saplings rarely, if ever, contain any heartwood and are easily impregnated throughout.

The usual procedure has been to inject three dozen air-dried saplings 3 feet in length with the preservative to be tested in a miniature treating plant using the full cell process. After discarding the butt 3 inches (7.62 cm.), the next 3 inches (7.62 cm.) are cut off for analysis, or for extraction and toximetry. (The preservative content tends to be higher in the upper part than in the butt. The same is significantly true for full-sized poles. However, in both cases we are interested chiefly in rates of depletion at the ground line which is nearer the butt.) A dozen of the saplings cut to a length of 30 inches (76.2 cm.) are set in the ground, butt down, in each of three test plots which are maintained at Limon, Colo.; Chester, N. J.; and Gulfport, Miss. Such quick and consistent results are obtained at the last-named location that the other test plots are now less used for this particular work. Comparative data at the three plots have, however, furnished a rough calibration of climatic influence on the test. Untreated saplings at Gulfport have always failed completely within a year either by rot or termite attack or both. All tests reported herein were made at the southern test plot.

The sapling form of specimen and its method of exposure is clearly imitative of a telephone pole. The contact with the soil and consequent leaching effect below ground and the exposure of the upper part of the sapling to the evaporative effects of the air are both essential features of the exposure. The data so obtained provide a well-rounded picture of the virtues and shortcomings for pole preservation purposes of each preservative. Naturally, the effects of ground water extend up into a sapling farther in proportion to its total length than is the case with a pole, so that one must be careful not to carry the parallelism too far in interpreting ground-line effects.

The specimens are examined for rot and insect attack at least once a year. On each inspection one or more from each group may be removed for laboratory examination. Chemical or biological assay of these saplings affords evidence

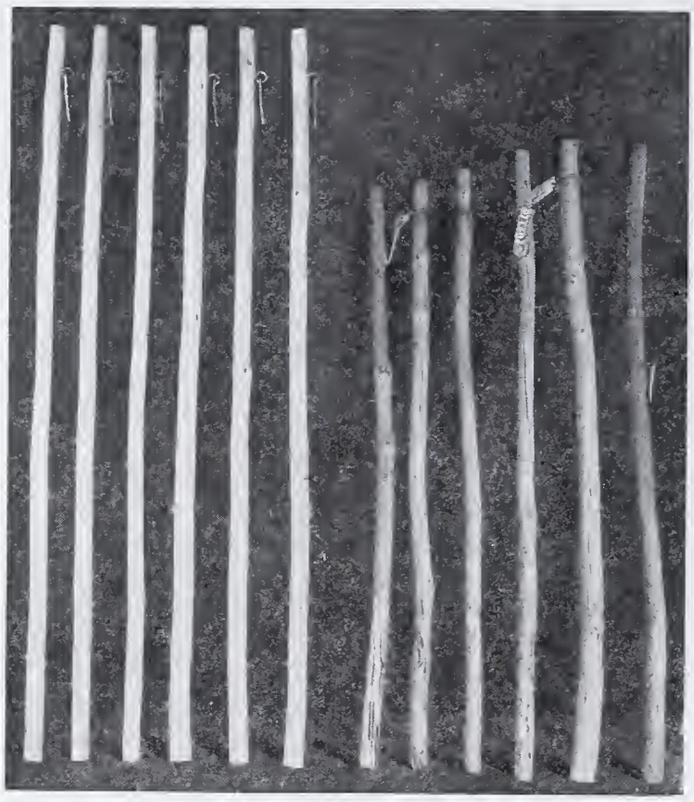

FIGURE 1. TREATED SAPLINGS

Left, freshly treated saplings, ready for analysis and subsequent exposure. Right, weathered saplings, showing decay and termite attack in butts.

of the rate of depletion and some indication of progress towards the decay stage. Within the first year, it is usually possible to tell by analytical means whether or not the material has promise. In extreme cases failure takes place during this period. Usually the less successful preservatives are attacked by insects or rot during their second year.

In order to save space the results of the field inspections have been shown in a graphic manner in Figures 3 to 8. The analytical results given in Tables I to V include with a few exceptions only those saplings which have been removed while still sound. The exceptions represent failures which had some special feature of interest. The analytical methods used have been described in a previous paper.[1]

[1] Waterman, Koch, and McMahon, IND. ENG. CHEM., Anal. Ed., 6, 409 (1934).

In Figures 3 to 8 each vertical line of squares represents the status of the group of saplings on the occasion of a particular inspection. Thus in series CU, Figure 3, at the end of 2 years, 2 saplings were broken or lost, 1 had been removed in a suspicious condition, and 1 had been removed in a sound state for analysis. Of the remaining saplings 5 were sound and 1 suspicious. The saplings are arranged in each vertical column in descending order of soundness, so that the cumulative extent of decay is seen at a glance as a massed cross hatching at the bottom of each series. The horizontal rows of squares therefore do not indicate the progress of decay in a particular specimen.

All concentrations of preservatives are stated in grams of preservative per 100 cc. of total wood volume. One gram per 100 cc. equals 0.625 pound per cubic foot.

Series marked "e" were impregnated by an empty-cell process, others by the full-cell process.

DISCUSSION OF RESULTS

Water-soluble salts have proved comparatively impermanent in the sapling tests (Figure 3), owing largely to the leaching out of the salts both above and below ground (Table I). The results with saplings are in harmony with commercial experience with poles correspondingly treated,

FIGURE 2. SAPLING TEST PLOT, GULFPORT, MISS.

in so far as the materials involved have had a commercial use in similar exposures. Mercury and copper treatments are more permanent in preventing decay of saplings than other soluble salts, thus conforming to the implications of the extensive and relatively satisfactory European experience with these salts in pole treatments. Probably some portion of the heavy metals is more or less definitely adsorbed on the fibers. Saplings treated with mercury and copper salts are

TABLE I. ANALYTICAL RESULTS ON SELECTED SPECIMENS USING "WATER-SOLUBLE" SALT TREATMENTS

Specimen Number	Years under Test	Original Concentration	Final Concentration Above ground line	Final Concentration Below ground line	Condition of Analyzed Specimen
		G./100 cc.*	G./100 cc.*		
		SERIES 1–16, ZINC CHLORIDE			
		As zinc	As zinc		
1	1	2.64	0.222	....	Sound
2	1	1.28	....	0.136	Sound
3	1	2.46	0.061	0.062	Sound
5	1	2.26	Nil	0.014	Rotted
6	1	2.50	0.056	0.053	Sound
8	2	2.46	0.053	0.029	Rotted
11	3	2.51	0.120	0.048	Termites
13	4	2.72	0.080	0.053	Rotted
15	2	2.05	0.093	0.043	Rotted
		SERIES C, ZINC CHLORIDE			
		As zinc	As zinc		
49	1	0.65	0.088	0.067	Sound
50	1	1.23	....	0.069	Sound
52	2	1.02	0.075	0.078	Sound
60	2	0.96	0.066	0.045	Slight decay
		SERIES BO, BORAX			
2	1	4.57	0.027	0.027	Rotted
15	1	4.43	0.066	0.013	Rotted
		SERIES IN, SODIUM FLUORIDE			
3	1	0.86	Nil	Nil	Termites
17	1	1.92	Nil	Nil	Termites
32	1	..	Trace	....	Termites
		SERIES AO, SODIUM ARSENITE			
		As As_2O_3	As As_2O_3		
3	1	0.90	0.0056	0.0021	Rotted
7	1	1.36	0.0035	0.0006	Rotted
10	1	1.26	0.0013	0.0011	Rotted
		SERIES AR, ARSENOUS ACID			
		As As_2O_3	As As_2O_3		
6	1	0.27	0.0042	0.0011	Sound
18	1	0.34	0.0048	0.0008	Rotted
		SERIES NA, PARTIALLY NEUTRALIZED SODIUM ARSENITE			
		As As_2O_3	As As_2O_3		
1	1	2.32	0.086	0.0043	Slight decay
2	1	2.40	0.030	0.0160	Sound
		SERIES CU, COPPER SULFATE			
		As copper	As copper		
3	1	0.77	0.118	0.045	Sound
5	2	0.64	0.048	0.056	Sound
7	2	0.50	0.102	0.062	Sound
10	1	0.45	0.077	0.088	Suspicious
		SERIES HG, MERCURIC CHLORIDE			
		As mercury	As mercury		
1	2	0.32	0.056	0.022	Sound
5	1	0.24	0.083	0.061	Sound
10	1	0.40	0.104	0.106	Suspicious

* 1 gram per 100 cc. = 0.625 lb. per cu. ft.

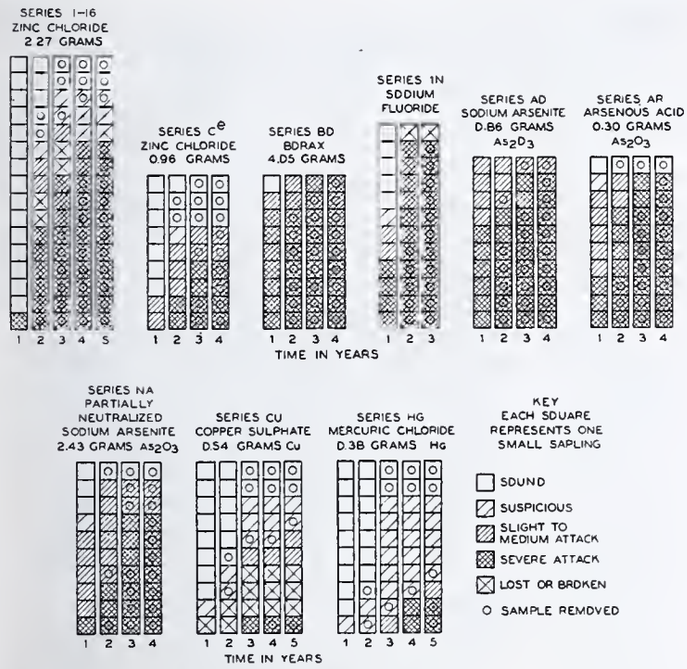

FIGURE 3. FIELD EXPOSURES OF SAPLINGS TREATED WITH WATER-SOLUBLE SALTS

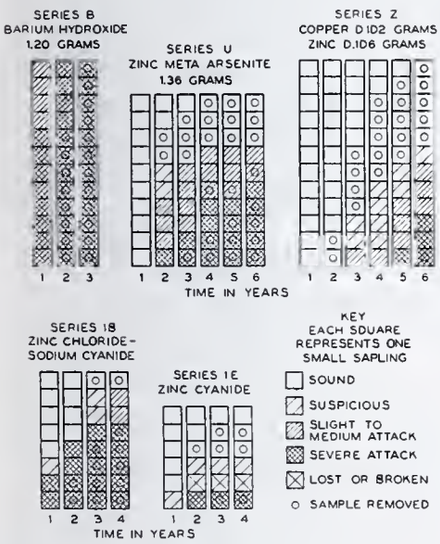

FIGURE 4. FIELD EXPOSURES OF SAPLINGS TREATED WITH WATER-INSOLUBLE SALTS

(15.23-cm.) diameter posts treated with solutions containing arsenous oxide and others treated with a partially neutralized solution of arsenous oxide (Figure 3) showed definite signs of decay after 4 years in the ground at the same site. The other water-soluble salts used in saplings were not tested by exposure of post specimens, as this class of salts was not considered sufficiently promising for long-life treatments to justify the expense of such tests.

Under "water-insoluble" salts various compounds are included which are used in water solution but afterwards tend to become sparingly soluble by evaporation of a constituent or by reaction with the air or the wood. The extent of losses by leaching is indicated in Table II and the evidence of permanence of resistance to decay in Figure 4. In noticeably brittle above ground line. Cotton treated with copper sulfate and dried has also been found to be markedly tendered. These facts are suggestive of a chemical action on cellulose in both wood and textile fiber.

In confirmation of the sapling results with the soluble arsenic compounds, it may be said that 6-inch the case of some preservatives the depletion as shown by analysis is marked; in others rot is observed in spite of the continued presence of substantial amounts of preservative.

TABLE II. ANALYTICAL RESULTS ON SELECTED SPECIMENS USING "WATER-INSOLUBLE" SALT TREATMENTS

Specimen Number	Years under Test	Original Concentration	Final Concentration Above ground line	Final Concentration Below ground line	Condition of Analyzed Specimen
		G./100 cc.*	G./100 cc.*		
		SERIES B, BARIUM HYDROXIDE			
6	1	1.31	0.54	0.42	Rotted
18	1	1.17	0.77	0.30	Rotted
		SERIES U, ZINC METAÄRSENITE			
		Zn basis / As basis	Zn basis / As basis	Zn basis / As basis	
3	1	1.12 / 1.15	0.30 / 0.172	0.14 / 0.078	Sound
4	1	1.13 / 1.18	0.64 / 0.166	0.46 / 0.109	Sound
6	2	1.39 / 1.41	0.90 / 0.178	0.64 / 0.075	Sound
		SERIES Z, AMMONIACAL SOLUTION OF COPPER AND ZINC HYDROXIDES			
		Cu / Zn	Cu / Zn	Cu / Zn	
5	1	0.115 / 0.107	0.083 / 0.094	0.072 / 0.056	Sound
6	1	0.101 / 0.107	0.083 / 0.085	0.082 / 0.080	Sound
8	2	0.102 / 0.096	0.086 / 0.056	0.082 / 0.026	Sound
9	2	0.097 / 0.101	0.078 / 0.058	0.075 / 0.038	Sound
24	3	0.101 / 0.112	0.102 / 0.063	0.112 / 0.016	Sound
		SERIES 1B, ZINC CHLORIDE–SODIUM CYANIDE			
		Zn	Zn	Zn	
2	2	0.294	0.138	0.085	Sound
10	1	0.271	0.222	0.186	Rotted
		SERIES 1E, ZINC CYANIDE			
		Zn	Zn	Zn	
5	1.5	0.484	0.339	0.191	Sound
12	2	0.442	0.365	0.230	Sound
16	1	0.544	0.370	0.193	Sound

* 1 gram per 100 cc. = 0.625 lb. per cu. ft.

The sapling results with two of the water-insoluble salts have also been checked by similar exposures at the same site of posts of 8-inch (20.6-cm.) diameter similarly treated in order to appraise further the merits of the sapling method of testing. Such posts, containing 0.48 gram of zinc metaärsenite per 100 cc. of total wood volume, lost about 80 per cent of the arsenic and about 40 per cent of the zinc below ground in 18 months. The losses above ground were much less. After 30 months, superficial decay was present below ground in 8 out of 14 posts; at 38 months, 13 showed some decay, 11 exhibiting disintegration up to a depth of 1 inch (2.54 cm.); at 60 months all showed decay; the only post removed for complete examination at this time showed rot throughout the sapwood at the butt. These results with posts are in reasonable agreement with those obtained with

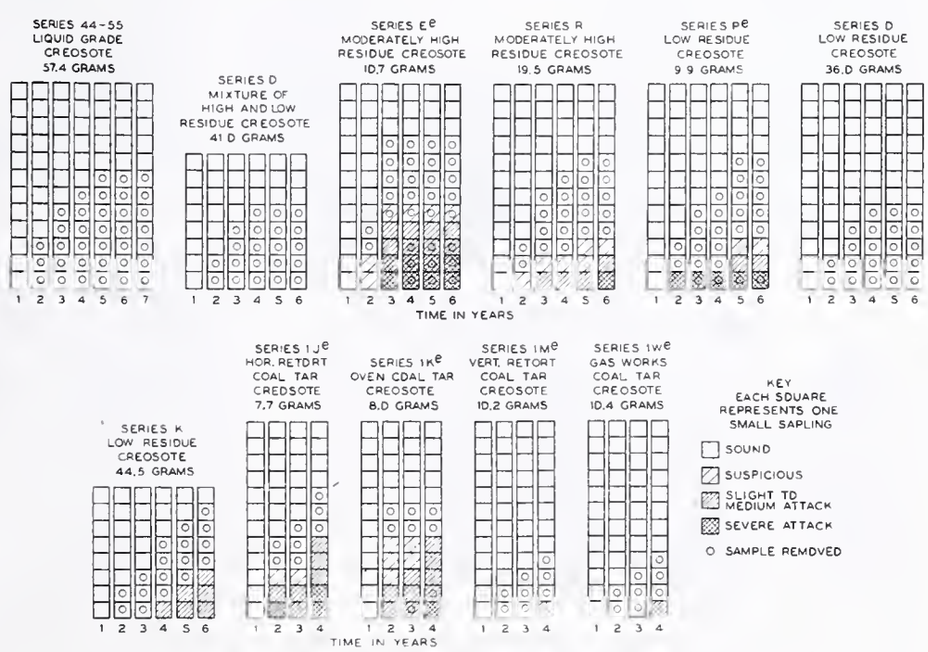

FIGURE 5. FIELD EXPOSURES OF SAPLINGS TREATED WITH COAL-TAR CREOSOTES

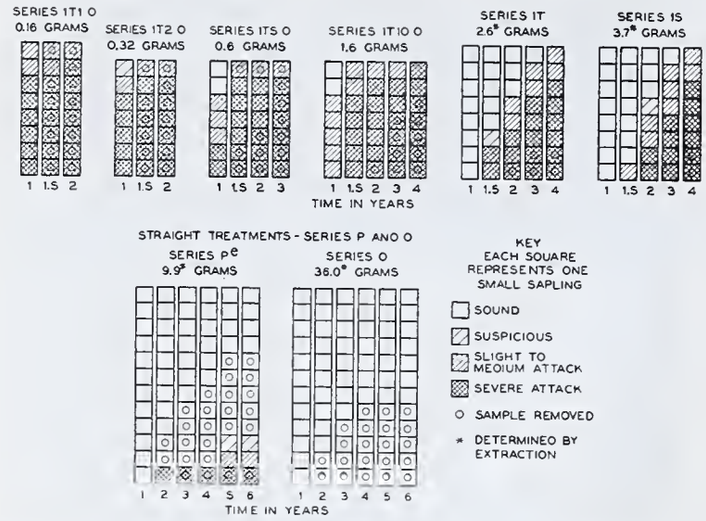

FIGURE 6. FIELD EXPOSURES OF SAPLINGS SHOWING EFFECT OF CONCENTRATION OF CREOSOTE

saplings (Figure 4). The relative life of the saplings has presumably been prolonged by the fact that they contained about 1.36 grams per 100 cc. of the preservative while the posts contained less.

On the other hand, posts treated with an ammoniacal solution of copper and zinc hydroxides (Figure 4, Series Z) decayed approximately as fast as saplings similarly treated. Among 25 posts exposed, 1 showed decay at the end of 2 years, 14 at 4 years, and 15 at about 7 years, the decay being largely below ground. In the case of saplings, evidence is given that loss of resistance is not due to extensive leaching of the metallic components (Table II, Series Z). The posts were also analyzed and showed little loss of copper or zinc over a period of 4 years. Decay is apparently due in both cases to gradual conversion of the hydroxides to the insoluble oxides which are very slightly toxic on account of their low solubilities. Such a reaction is very little influenced by the size of the piece and the behavior of the saplings must be regarded as consistent with that of the posts in this instance also. These incidents, however, make clear the

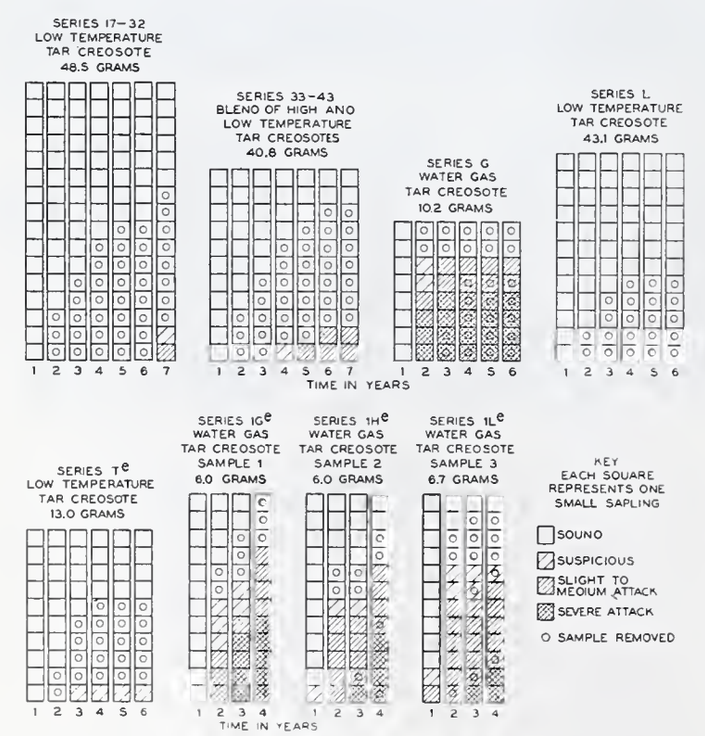

FIGURE 7. FIELD EXPOSURES OF SAPLINGS TREATED WITH VARIOUS CREOSOTES

TABLE III. ANALYTICAL RESULTS ON SELECTED SPECIMENS USING COAL-TAR CREOSOTE TREATMENTS

Specimen Number	Years under Test	Original Concentration	Final Concentration Above ground line	Final Concentration Below ground line	Condition of Analyzed Specimen
		G./100 cc.*	G./100 cc.*		
SERIES 44–55, LIQUID CREOSOTE					
44	1	60.6	42.8	54.6	Sound
45	1	59.8	31.2	50.0	Sound
46	1	44.2	27.3	49.5	Sound
47	2	50.9	31.2	33.3	Sound
48	2	57.0	42.8	41.7	Sound
49	3	52.4	27.2	45.4	Sound
55	4	49.8	35.8	24.5	Sound
SERIES D, MIXTURE OF HIGH- AND LOW-RESIDUE CREOSOTES					
17	1	30.7	29.3	18.1	Sound
18	1	51.6	45.3	50.0	Sound
20	2	41.2	21.6	28.0	Sound
21	2	31.5	24.2	24.6	Sound
28	3	55.4	18.4	26.8	Sound
SERIES E, MODERATELY HIGH-RESIDUE CREOSOTE					
1	1	8.5	5.3	4.3	Sound
3	1	5.6	1.9	3.5	Sound
4	2	10.1	5.4	4.8	Sound
9	2	8.6	4.2	4.5	Sound
11	3	10.1	5.6	6.1	Rotted
21	3	12.6	3.4	2.6	Suspicious
SERIES R, MODERATELY HIGH-RESIDUE CREOSOTE					
1	1	24.2	17.1	15.8	Sound
3	1	17.3	7.0	10.6	Sound
4	2	14.5	10.1	9.4	Sound
5	2	16.3	9.1	12.1	Sound
24	3	15.5	7.7	5.3	Sound
SERIES P, LOW-RESIDUE CREOSOTE					
6	1	9.1	7.2	3.7	Sound
7	1	10.8	5.8	5.6	Sound
8	2	14.7	2.9	2.4	Sound
10	2	14.2	4.8	3.8	Sound
SERIES O, LOW-RESIDUE CREOSOTE					
1	1	22.5	26.2	28.2	Sound
6	1	26.3	15.6	15.8	Sound
9	2	45.4	27.1	25.0	Sound
13	2	46.1	10.7	19.9	Sound
22	3	45.0	19.1	21.1	Sound
SERIES K, LOW-RESIDUE CREOSOTE					
33	1	54.1	41.1	39.4	Sound
34	1	48.2	37.1	36.8	Sound
38	2	48.8	20.5	18.9	Sound
43	3	50.6	16.8	24.5	Sound
SERIES 1J, HORIZONTAL RETORT COAL-TAR CREOSOTE					
1	2	7.4	2.6	1.8	Sound
34	1	7.7[a]	5.5	4.8	Sound
36	1	7.7[a]	4.3	4.3	Sound
SERIES 1K, OVEN COAL-TAR CREOSOTE					
9	2	5.6	2.4	2.1	Slight decay
32	1	8.0[a]	5.3	6.9	Sound
35	1	8.0[a]	5.6	6.1	Sound
SERIES 1M, VERTICAL RETORT COAL-TAR CREOSOTE					
3	2	9.0	3.4	3.0	Sound
33	1	10.1[a]	8.2	6.4	Sound
35	1	10.1[a]	7.4	5.8	Sound
SERIES 1W, GASWORKS COAL-TAR CREOSOTE					
7	2	9.3	4.2	3.4	Sound
30	1	10.4[a]	9.0	7.8	Sound
34	1	10.4[a]	6.1	5.0	Sound

* 1 gram per 100 cc. = 0.625 lb. per cu. ft.
[a] Average of charge.

necessity of supplementing the exposure of saplings by periodic analyses to secure a true interpretation of results.

OILS

Experimental work on oily preservatives has been greatly complicated by difficulties of control of the amount of preservative introduced into the saplings. Some of the earlier series, such as 17 to 32, Figure 7, and 44 to 55, Figure 5, were full-cell treated and contain so much creosote that they will, when the experiment is finished, merely serve to indicate how long saplings can be preserved with large amounts of creosote. Such results will have some value as a norm of extremely good preservation and to illustrate the loss of creosote from wood exposed to the weather. Later empty-cell methods were used with somewhat better success. However, some experiments, such as O and R, Figure 5, still failed because of lack of control of retent to bring out satisfactorily the comparison which was intended—in this case that of one kind of creosote with another kind. There has

Table IV. Analytical Results on Selected Specimens Using Water-Gas and Low-Temperature Tar Creosote Treatments

Specimen Number	Years under Test	Original Concentration	Final Concentration Above ground line	Final Concentration Below ground line	Condition of Analyzed Specimen
		G./100 cc.*	G./100 cc.*		
Series 17–32, low-temperature tar creosote					
17	1	48.5[a]	15.8	21.8	Sound
18	1	46.9	23.8	34.9	Sound
19	1	41.9	16.8	25.1	Sound
20	2	45.1	20.3	30.2	Sound
21	1	54.1	24.8	29.3	Sound
22	3	55.5	15.8	16.5	Sound
23	3	52.2	19.4	22.4	Sound
32	4	51.7	17.4	5.8	Sound
Series 33–43, blend of high- and low-temperature tar creosotes					
33	1	47.7	31.4	28.6	Sound
34	1	34.9	14.9	19.7	Sound
35	1	35.7	22.6	31.7	Sound
37	2	53.0	22.6	33.6	Sound
38	3	31.8	24.0	18.4	Sound
43	4	41.4	21.9	30.2	Sound
Series G, water-gas tar distillate					
3	1	5.7	1.3	1.8	Sound
5	1	8.6	1.1	1.9	Sound
7	3	5.1	0.9	1.0	Rotted
Series L, low-temperature tar creosote					
1	1	49.9	57.0	53.3	Sound
2	1	53.6	58.2	54.5	Sound
3	2	60.0	34.2	47.3	Sound
5	2	46.6	30.2	43.7	Sound
22	3	34.5	34.7	31.2	Sound
Series T, low-temperature tar creosote					
4	1	12.5	10.7	11.4	Sound
5	1	11.2	13.1	11.4	Sound
6	2	16.3	14.1	8.6	Sound
8	2	8.8	6.1	3.5	Sound
19	3	19.2	6.1	3.8	Sound
Series 1G, water-gas tar distillate					
10	2	5.3	2.9	0.6	Sound
29	1	5.9[a]	5.1	3.8	Sound
30	1	5.9[a]	3.2	2.6	Sound
Series 1H, water-gas tar distillate					
1	2	5.6	3.1	0.8	Slight decay
26	1	5.9[a]	3.7	1.8	Sound
27	1	5.9[a]	2.2	2.1	Sound
Series 1L, water-gas tar distillate					
4	1	6.1	2.7	0.4	Slight decay
8	2	5.8	3.2	1.9	Sound
35	1	6.7[a]	4.2	1.8	Sound
36	1	6.7[a]	9.0	3.8	Sound

* 1 gram per 100 cc. = 0.625 lb. per cu. ft.
[a] Average of charge.

Table V. Analytical Results on Selected Specimens Using Treatments with Special Oils, Mixtures, etc.

Specimen Number	Years under Test	Original Concentration	Final Concentration Above ground line	Final Concentration Below ground line	Condition of Analyzed Specimen
		G./100 cc.*	G./100 cc.*		
Series F, tar acid freed creosote					
1	1	19.7	23.4	21.0	Sound
2	1	58.6	26.6	23.2	Sound
3	2	33.5	19.4	13.3	Sound
4	2	49.2	12.6	15.4	Sound
22	3	23.4	11.7	10.1	Sound
Series X, creosote–crude oil mixture					
1	1	50.0	45.8	44.8	Sound
2	1	51.0	21.9	21.6	Sound
3	2	48.7	45.2	42.0	Sound
4	2	51.7	42.7	44.3	Sound
12	3	34.3	31.4	28.0	Sound
Series M, 60–40 wax-creosote mixture					
14	1	..	6.4	5.0	Sound
15	1	8.7	5.1	5.9	Sound
Series WT, wood-tar creosote					
1	1	25.8	17.9	14.4	Sound
2	1	17.8	12.3	10.4	Sound
10	2	27.0	12.5	10.7	Sound
Series WE, wood-tar creosote					
2	1	7.7	5.8	3.7	Sound
4	1	9.3	5.3	4.2	Sound
5	2	9.8	5.1	2.7	Sound
Series CN, crude oil–naphthalene					
3	1	35.7	28.0	29.6	Sound
5	2	50.6	26.9	18.6	Sound
9	1	40.3	26.2	30.1	Sound
Series CA, crude oil–naphthalene–anthracene					
1	1	24.0	35.4	23.8	Sound
3	1	17.6	21.6	18.1	Suspicious
10	2	25.6	43.5	25.1	Suspicious
Series CG, water-gas tar					
1	1	27.5	29.1	25.3	Sound
2	1	26.7	21.9	25.9	Sound
10	2	26.7	23.4	17.9	Sound
Series CE, water-gas tar					
4	1	11.2	11.0	5.0	Sound
7	1	9.3	3.2	2.7	Sound
10	2	9.9	3.0	2.7	Sound
Series PG, water-gas tar					
1	1	34.6	31.8	18.5	Sound
2	1	28.0	26.9	19.9	Sound
10	2	44.2	16.3	19.0	Sound
Series PE, water-gas tar					
6	2	7.7	5.1	4.3	Sound
8	1	8.0	7.2	6.4	Sound
10	1	10.2	11.7	5.1	Sound

* 1 gram per 100 cc. = 0.625 lb. per cu. ft.

been a constant effort to standardize an empty-cell process of impregnating saplings with oil, but experience shows that the same treatment with two oils of different composition often results in dissimilar retents. The authors believe that this is primarily due to differences in viscosity of the oils manifesting themselves in the kick-back and pull-back stages of the empty-cell treatment. Oils of lesser viscosity are removed more completely during these steps.

Further experiments at length developed a process which promises to be satisfactory. This involves the use of a toluene solution of the creosote to be examined, so that a full-cell treatment, such as was used with salts, can be employed without leading to excessively large retents. In Figure 6 are shown the results over a period of 2 years of the exposure of six series of saplings treated with toluene solutions of a single creosote in graduated concentrations. In this way, a gradation of retent is assured which makes for better uniformity and better comparability. It also serves to accelerate the test further, since some information about the quality of a creosote can be obtained in less than 1 year's time by observing its effects in low concentrations. Simultaneous experiments with larger amounts serve to afford further accumulations of evidence from year to year. The toluene evaporates quickly and does not seem to influence the results of exposure. The toluene dilution method is now

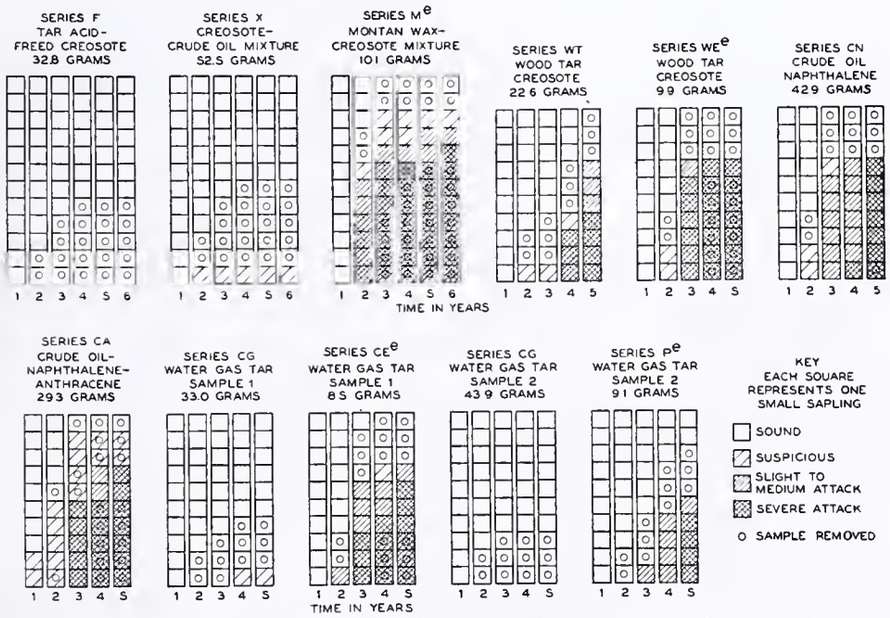

Figure 8. Field Exposure of Saplings Treated with Special Oils, Mixtures, etc.

TABLE VI. ANALYSES OF COAL-TAR CREOSOTES

Series	44–55	D	E, R	K	O, P, 1T1D-1S	1J	1K	1M	1W
Specific gravity at 38°/15° C.	1.095	1.077	1.093	1.061	1.060	1.059	1.065	1.068	1.046
Benzene-insoluble, %	0.09	...	0.14	0.47	0.38	0.25	Trace	Nil	0.09
Distillation, ° C.									
0–170	0.43	0.53	0.76	0.36	1.21	0.00	0.00	0.00	0.04
170–205	1.30	1.38	1.70	0.43	3.44	0.24	1.56	0.71	4.53
205–210	0.31	0.35	0.36	0.27	2.68	0.62	1.35	0.69	3.34
210–235	2.12	16.61	4.63	19.39	23.31	9.17	11.02	8.00	18.51
235–245	1.39	9.26	4.53	10.73	7.52	9.01	6.58	5.91	4.48
245–270	9.35	12.85	11.10	15.34	11.80	16.49	13.46	12.23	10.68
270–300	16.37	6.98	8.97	11.34	5.81	12.30	11.79	12.30	7.83
300–315	10.81	3.16	5.85	5.87	8.12	5.36	6.66	6.04	6.95
315–355	35.91	12.44	23.19	17.36	18.49	23.15	24.57	20.80	18.77
Residue above 355	21.97[a]	36.31	38.83	18.86	17.43	23.12	22.74	33.06	24.31
Total	99.96	99.87	99.92	99.95	99.81	99.46	99.73	99.74	99.44
Tar acids, 0–300° C., %	2.0	2.5	3.6	5.5	6.4	5.6	5.9	11.3[b]	11.6[b]
Sulfonation residue, % of 300–355° C. fraction	0.1	1.7	0.5	1.3	0.5	2.1	0.9	1.3	3.2

[a] Distillation carried to 360° C.
[b] Domestic creosotes of foreign type.

TABLE VII. ANALYSES OF WATER-GAS AND LOW-TEMPERATURE TAR CREOSOTES

Series	17–32	33–43: 1 part[a]	33–43: 3 parts	G	L, T	1G	1H	1L
Specific gravity at 38°/15° C.	0.983	1.037	0.999	1.015	1.011	1.020	1.021	1.018
Benzene-insoluble, %	0.04	0.50	0.06	0.04	...	Nil	0.07	0.16
Distillation, ° C.								
0–170	2.14	0.67	0.53	1.28	2.47	0.00	0.00	0.00
170–205	1.96	2.00	0.34	2.11	2.56	1.05	2.63	1.76
205–210	2.83	1.47	0.04	0.36	0.49	1.71	2.43	1.12
210–235	30.14	27.94	6.33	15.99	9.03	12.74	12.62	13.70
235–245	9.08	9.29	14.00	14.39	4.74	11.15	14.42	8.95
245–270	16.18	13.47	25.46	30.03	13.99	23.00	21.09	21.44
270–300	14.91	12.44	21.84	16.27	9.18	14.96	14.07	14.46
300–315	5.47	6.55	7.74	6.30	7.20	5.32	4.71	14.60
315–355	10.64[b]	15.04[b]	16.16[b]	8.48	25.41	11.77	13.66	6.02
Residue above 355	6.51	10.68	7.34	4.69	24.82	17.29	13.66	17.54
Total	99.86	99.55	99.78	99.90	99.89	98.99	99.29	99.59
Tar acids, 0–300° C., %	32.4	8.3	25.0	0.7	19.2	Trace	Trace	0.3
Sulfonation residue, % of 300–355° C. fraction	14.6	3.2	11.5	0.6	14.8	3.0	1.0	3.5

[a] A "regular" creosote.
[b] Retort used in distillation which was carried to 360° C.

TABLE VIII. ANALYSES OF SPECIAL OILS, MIXTURES, ETC.

Series	F	M, X	CG, CE	PG, PE	WT, WE
Specific gravity at 38°/15° C.	1.075	For creosote used see Series K	1.067	1.065	1.065
Benzene-insoluble, %	0.02		1.11	3.98	...
Distillation, ° C.					
0–170	0.09		1.24	0.65	0.88
170–205	0.43		4.65	0.29	1.83
205–210	0.10		1.78	0.10	1.12
210–235	6.60		15.03	5.39	35.83
235–245	11.60		7.03	7.64	13.14
245–270	19.63		11.74	14.53	21.63
270–300	13.98		7.56	11.69	14.98[a]
300–315	6.09		3.40	4.36	...
315–355	20.52		13.56	16.04	...
Residue above 355	20.88		33.66	39.05	9.87[a]
Total	99.92		99.65	99.74	99.28
Tar acids, 0–300° C., %	0.3		Nil	0.4	57.7[a]
Sulfonation residue, % of 300–355° C. fraction	1.5		0.6	8.6	...
Coke test, %	...		12.47	14.97	...
Float test, seconds	...		>600	>600	...

[a] Distillation ceased at 289° C.

preferred for general use in comparing the quality of oil preservatives. The six series referred to in Figure 6 give excellent evidence of the effect of quantity of creosote, as do also series P and O included in the same chart and E and R in Figure 5.

Figures 5 to 8, inclusive, show the results up to the present time of numerous variations in the kind and quantity of preservative mixture. Some of these experiments have not progressed far enough to be conclusive; others are somewhat impaired by the lack of precise control of quantity which has already been mentioned. Nevertheless, the results shown in these charts and in Tables III to V, inclusive, are believed to indicate clearly the possibility of distinguishing between a good and bad preservative with considerable precision and in a much shorter time than is possible with an actual service test. Analyses of the oil preservatives used are given in Tables VI to VIII. The water-gas products mentioned in Figures 7 and 8 were kindly furnished for test by reputable suppliers who vouched for their authenticity.

It should be borne in mind that the primary purpose of the sapling test is to indicate the relative merits of various preservatives from the standpoint of permanence in poles. For this purpose it has great promise. Perhaps it will never be possible to predict pole life in absolute terms from the sapling results, but further experience may yield a more quantitative measure than we now have of the degree of acceleration achieved by use of the sapling. This specimen is not well adapted to studies of methods of treatment or of extent of penetration, factors which are known to be extremely important in full-size timber; nor can the results of sapling tests be accepted with equal assurance with respect to the preservation of other timber than poles and posts. However, for the limited purpose for which it was designed the sapling test method appears to have a distinct field of usefulness.

It is hoped that it will be possible to report further in a year or two with regard to the results of continuance of the exposures already mentioned and of others which have been started more recently. At that time, a discussion may be warranted of the significance of the results for the choice of preservatives.

RECEIVED April 14, 1934.

RESEARCH on lithographic papers, carried on jointly by the National Bureau of Standards and The Lithographic Technical Foundation for a number of years until July, 1933, when it was discontinued because of lack of funds, has been resumed at the bureau under the research associateship plan.

Indiana Oxidation Test for Motor Oils

T. H. Rogers and B. H. Shoemaker, Standard Oil Company (Indiana), Whiting, Ind.

In a paper (*2*) presented at the September, 1933, S. A. E. meeting it was shown that the oxidation stability of motor oils is an important characteristic, particularly in heavy-duty service. A comprehensive series of engine tests was made in which the changes taking place in a wide variety of oils were measured. Several types of oxidation tests were made on the same oils and it was found that a test using air at 341° F. (171.7° C.) gave the best correlation with the engine performance tests. In view of the rather general interest in this laboratory test (known as the Indiana oxidation test) it appears desirable to present in greater detail the procedure as well as the influence of various factors in the test.

Upon oxidizing motor oils at relatively high temperatures it is generally found that no insoluble oxidation products form during an initial period, after which asphaltene formation takes place at an increasing rate, this behavior often being known as sludging. The Indiana oxidation test measures the length of time (sludging time) until rapid formation of asphaltenes begins, as indicated by an asphaltene content of 10 mg. per 10 grams of oil. In addition, as a measure of the rate of sludging, the time required to form a larger amount of sludge (100 mg. per 10 grams) is also determined. Motor oils vary widely in their oxidation stability—from 10 or 15 up to several hundred hours' sludging time—those of lighter grades having, in general, lower stabilities than the heavier grades. For oils of certain types which have little or no tendency to form asphaltenes, it becomes more desirable to measure the rate of viscosity increase for which the test procedure makes provision. In general, on the basis of work previously described, for oils having a sludging time above about 100 hours, determination of the viscosity increase becomes more significant than sludging time and a sludging rate.

The apparatus used for the Indiana oxidation test, with the exception of the glass flowmeters, is shown in Figure 1, and the test in standardized form as used by various laboratories of the Standard Oil Co. (Indiana) is described below.

Method

Apparatus. A thermostatically controlled oil bath suitable for immersion of the oil tubes to a depth of 30 cm. Bright stock of good stability is used for the bath. Temperature regulation at approximately 342° F. (172.2° C.) within ±0.5° F. must be maintained. Oil tubes must be placed symmetrically with reference to stirrer and heater.

Oil test tubes of heat-resistant glass of 40 to 44 mm. inside diameter, 450 to 500 mm. long, provided with a slotted cork stopper into which is fitted an air delivery tube of glass, of 4 to 5 mm. inside diameter.

Flowmeters, calibrated in liters of air per hour, through which air at constant pressure is supplied.

Procedure. Determine the observed bath temperature which must be maintained in order to keep the test oil at a temperature of 341° ± 0.5° F. (171.7° C.), corrected. Take the temperature of the test oil with the tube in place, containing 300 cc. of oil, while passing through air at a rate of 10 liters per hour. Use a standardized thermometer, immersing it to the approximate center of the oil, and make appropriate stem correction. Having established this comparison of bath and test oil temperature, the observed bath temperature may be used for control so long as the rate of stirring of the bath is not markedly varied and the viscosity of the bath oil has not increased to more than 200 seconds Furol at 210° F. (98.9° C.).

Fill the oil tube to a depth of 23 cm. (approximately 300 cc. of oil.) Place the tube in the bath, the level of which must be at least 5 cm. above that of the test oil. The oil bath must be up to temperature and be so maintained that the temperature of the test oil is 341° ± 0.5° F. The air delivery tube is placed so that the end is within 6 mm. of the bottom of the oil tube. One-half hour after placing the oil in the bath, start the air at a rate of 10 ± 1 liters per hour (as measured under laboratory conditions). The start of the test period is the time of starting the air.

For determination of sludge values withdraw a 25-cc. sample of the test oil in a pipet. Weigh 10 grams (± 0.1 gram) of this portion immediately into a 300-cc. Erlenmeyer flask, and dilute with 100 cc. of A. S. T. M. precipitation naphtha (*1*). The naphtha used must, by comparative test on a sample of oxidized oil, give within 25 per cent of the sludge value obtained with a reference sample of A. S. T. M. precipitation naphtha. Stopper the flask and allow the solution to stand for 3 to 3.5 hours at room temperature (70° to 85° F., 21.1° to 29.4° C.).

Prepare a Gooch type crucible (approximately 35 mm. in diameter) with a mat of 0.5 to 0.65 gram of medium asbestos fiber. During preparation of the mat, press it down before adding the last portion. Dry the crucible at approximately 300° F. (148.9° C.) for at least 2 hours in an oven and weigh. Filter the sample, wash with precipitation naphtha, heat at approximately 300° F. for 0.5 hour, and weigh. Express the sludge as milligrams per 10 grams of oil.

Samples for sludge determination may be taken every 24 hours before sludging begins. Take at least three samples, giving sludge values between 5 and 125 mg., including one between 5 and 20 and one between 50 and 125. A plot of these values *vs.* time on log paper is then used to determine the sludging time and the 100 mg. time. For tests made at barometric pressures differing by more than 5 per cent from one atmosphere, correct these times to normal barometric pressure by multiplying the observed time by the ratio of the barometric pressure during the test to 760.

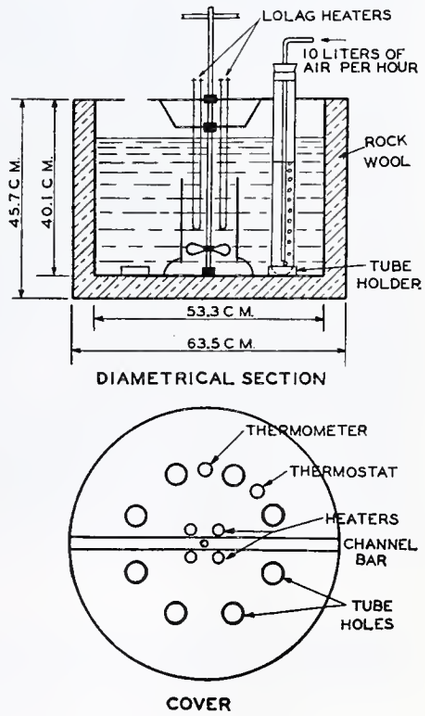

Figure 1. Diagram of Apparatus

For determination of viscosity increase, samples of approximately 75 cc. are withdrawn every 50 hours and used to run a Saybolt viscosity. This oil is then replaced in the test tube.

Factors Affecting the Oxidation Test

Significant factors in connection with the Indiana oxidation test are:

Temperature Control. In view of the relatively steep temperature coefficient of the reaction, accurate temperature control is obviously necessary and it is important to use a standardized thermometer and make proper stem correction. Aside from faulty bath control, irregularities may be caused by the bath oil becoming too viscous, thus causing greater differential between bath and test oil temperature.

Air Rate. Under the conditions employed, an excess of oxygen is provided and very precise measurement of air rate is not essential. However, marked variation from the standard air rate, particularly on the low side, will appreciably affect the sludging time.

Barometric Pressure. As shown by Table I, the sludging time varies inversely with the partial pressure of oxygen.

Table I. Influence of Barometric Pressure

	Pressure	Oxygen Supply[a]	Asphaltenes Formed 10 Mg.	100 Mg.
	Mm.		*Hours*	*Hours*
1	Atmospheric (750)	Air	64.5	95.5
2	Atmospheric (750)	80% air, 20% N_2	81	115
3	840	Air	58	88

[a] In each case the rate was 10 liters per hour at the pressure in question.

This relationship apparently holds only over relatively narrow limits, as the use of 100 per cent oxygen gives results which do not bear a constant relationship to those with air on a wide variety of oils.

Settling of Sludge in Oil Tube. It is obviously necessary to obtain a homogeneous sample and the stirring afforded by the air delivery facilitates this. It is important that the air tube extend to the bottom of the tube as provided.

Precipitation Naphtha. Although the data are rather incomplete, it is indicated that variations within the A. S. T. M. specifications for precipitation naphtha may cause marked irregularity in asphaltene determinations. For example, with two naphthas, each of which met the requirements for gravity and distillation points, having aniline points of 59.0° and 57.6° C. (A. S. T. M. specification is 58° to 60° C.) differences of several fold in the asphaltene determination on the same sample of oxidized oil were obtained. This caused a difference of 5 hours (7 per cent) in the apparent sludging time as between the results obtained with the two naphthas. For this reason the standardization of the naphtha against a reference sample, arbitrarily adopted as a standard for one or more laboratories is recommended.

Time of Standing. Variations in the time of standing of the naphtha solution before filtering may cause pronounced differences with stable oils, particularly at low asphaltene concentrations. Observations show that the sludging time may be decreased by as much as 5 hours on increasing the time of standing from 3 to 18 hours.

Filter. Variations in the mat thickness and area will affect the amount of asphaltenes obtained from a given sample. This appears to be due to adsorption as well as to incomplete separation of the finely divided solids. For this reason the amount of asbestos and the area of the filter are kept constant.

Reproducibility

Using the test as described above, agreement within a range of 10 per cent of the sludging time can be obtained by different operators. Duplicate determinations by the same operator show much closer agreement. Table II shows data obtained in different apparatus and by different operators.

Table II. Reproducibility of the Indiana Oxidation Test

Oil	Apparatus		Asphaltenes Formed 10 Mg.	100 Mg.
			Hours	*Hours*
I	A		62.5, 63	93, 93
I	B		64.5, 65, 62.5	99, 99, 96
I	C		66, 66	
I	D		65	95
I	E[a]		65.5, 65	
		Av.	64.5	96
II	A		56	..
II	C		56	..
II	D		54	..
II	E[a]		60	..
		Av.	56.5	

[a] Observed values for oil I were 76.5 and 77; 70 hours for oil II. These values were corrected for an observed barometric pressure of 650 mm.

Literature Cited

(1) Am. Soc. Testing Materials, Section 6(a), Method D91–33, A. S. T. M. Standards, Part II, 1933.
(2) Barnard, Barnard, Rogers, Shoemaker, and Wilkin, *S. A. E. Journal*, 34, 167 (1934).

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Flame Determination of Copper by Carbon Tetrachloride

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The usual method of determining copper compounds and alloys is to place the substance to be tested on a clean platinum wire and insert it in the inner part of the flame. If copper is present, the outer flame is colored green, but this is not a definite test for copper because many other elements burn with a green flame. The test is more delicate if the substance is soaked with hydrochloric acid, when copper colors the outer flame azure-blue with tinges of green. However, this test is subject to interference of other elements, it is inconvenient and not clean, and the receptacle which contains the hydrochloric acid must be cleaned after every test to avoid impurities which may spoil further tests.

If a copper compound or alloy is placed in the flame, the whole flame is colored blue when chlorine is passed through the draft of the Bunsen burner. Other elements which burn with a green flame are not affected by the chlorine. The chlorine method is much more effective than the acid method, but is more troublesome.

Carbon tetrachloride has the same effect as chlorine upon the color of the flame, and the test requires only a piece of cotton soaked with carbon tetrachloride placed in a small receptacle attached to the Bunsen burner.

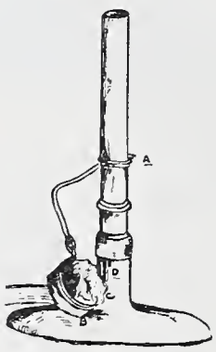

Figure 1. Apparatus for Flame Determination

A, wire twisted around burner for grip
B, small receptacle
C, cotton soaked with carbon tetrachloride
D, draft of Bunsen burner

The flame always turns blue when copper is present, but with a minute amount of copper it is sometimes necessary to moisten the substance with water and juggle it in the flame, to find the best part for that particular substance—usually the tip of the flame.

The amount of copper present and the other elements with which the copper is united determine the length of time the substance should remain in the flame. The flame usually turns blue immediately, even with minute amounts. In the case of copper telluride, nearly a minute is required before the appearance of the blue color, and even when the blue color appears traces of green can be seen in the flame, caused by the presence of tellurium.

The same test can be applied to calcium, and is even more delicate because in this case the flame turns from reddish orange to red. The change of color in the flame must be carefully noted when dealing with compounds of calcium.

Received August 25, 1934.

An Evaporation Rate Method Applied to Petroleum Thinners

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THE method in most general use for expressing the volatilities of solvents and thinners is graphical (*4*, *5*, *7*, *9*), plotting per cent liquid remaining, or per cent evaporated, against time elapsed. No satisfactory substitute for graphical representation of the volatility of heterogeneous liquids such as naphthas and the less pure grades of solvents has been devised or proposed, as no other method shows the change in volatility as the liquid evaporates. Most of the work in this field has been towards refining the procedure for obtaining these "loss in weight–time elapsed" curves (*1*, *3*, *4*, *6*, *8*).

Perhaps the most popular vessel used today in running evaporation curves is a small metal pan, often simply the lid from a friction-top can (*4*). In order to lessen errors due to stray air currents Wilson and Worster (*10*) suggested that during evaporation the pans be kept in a small wooden tunnel. The Hart balance (*6*) avoids the troublesome manipulation of the analytical balance. Ivanovszky (*8*) describes a recording balance for drawing evaporation curves. In order to avoid variations in data due to cooling of the liquid by evaporation and the effect of stray air currents, some laboratories suspend the evaporation vessel from a Jolly balance (*4*), supported in a celluloid chimney.

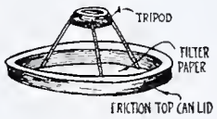

Figure 1. Apparatus

The friction-top can lids, at present widely used, have one limitation in common with the Petri dish method (*4*). The flat bottom is unevenly wetted towards the end of the evaporation, causing a decrease in size of the evaporating surface. This gives an undue flattening of the curve towards the end of the evaporation and a false final dry time. Bridgeman (*1*) proposes to eliminate this uneven wetting by using pans with a slightly dished bottom, so that equal volume of liquids will have equal evaporating surfaces.

By a method developed in this laboratory a constant evaporation surface was apparently maintained, and the evaporation was allowed to proceed under conditions closely duplicating actual use of solvent in industry. When C. P. material was evaporated by this method, a straight-line evaporation curve was obtained. A method which gives a straight-line evaporation curve for C. P. compounds should give a true representation of the evaporation curve of a petroleum thinner.

Development of Method. The use of a dished container overcame the difficulty of the uneven wetting of the bottom of a pan with a flat inner surface, but caused a change in the evaporation surface area of the liquid and a subsequent elongation of the evaporation curve as dryness was approached. It is desirable to have the surface constant to the end of the evaporation, since these data are to be used in studying the behavior of the liquids in films from which they evaporate from a constant surface.

It was found that the objection to the use of a flat-bottomed pan was made less by putting into the pan a piece of high-grade filter paper, cut to fit into the bottom of the pan with its edges just barely touching the sides. Theoretically, a pure substance should give a straight-line curve, provided the evaporating surface remains constant, since in such a liquid no physical characteristic will change during the course of evaporation. Evaporation curves of C. P. benzene and C. P. toluene run by this method, although greatly improved, still showed a slight variation from the straight-line evaporation desired, apparently caused by a bellying or lifting of the filter paper from the bottom of the pan as dryness was approached. This was overcome by placing in each pan a small wire-legged tripod (total weight approximately 10 grams). Evaporation curves, run from pans containing filter paper and tripod weights, on C. P. benzene and C. P. toluene showed that these compounds evaporate in a straight line.

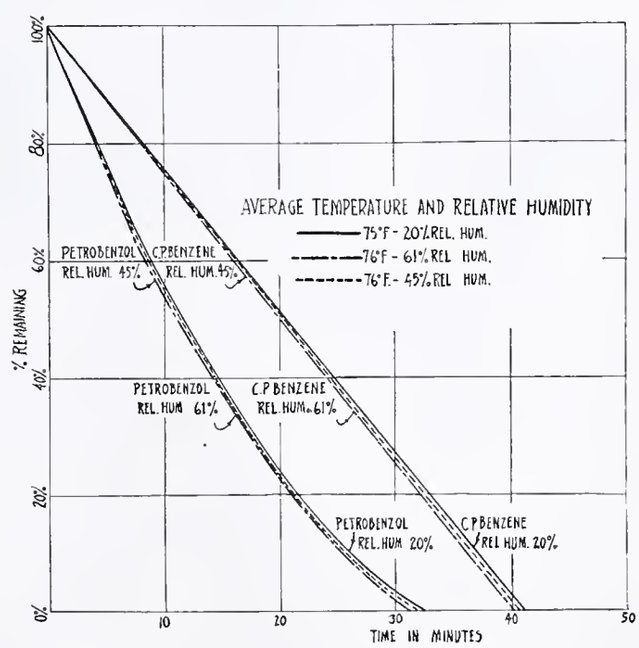

Figure 3. Evaporation Curve

Apparatus and Procedure. The pans used in these tests were ordinary friction-top can lids (Figure 1), measuring about 6.5 cm. in diameter (inside) and 0.75 cm. in depth. Munktell's Swedish filter paper No. 0 was used. The tripod weights were simple affairs, merely three wire legs and a small weight at the apex, and were built low enough so that they were not easily tipped over, those used in these tests being 3 cm. high. The wire legs were made so that the tripod rested on the edge of the filter paper in the pan, with lower ends rounded so as not to pierce the filter paper. In these 3 cc. of liquid were used, this being a convenient volume for the size of the pan.

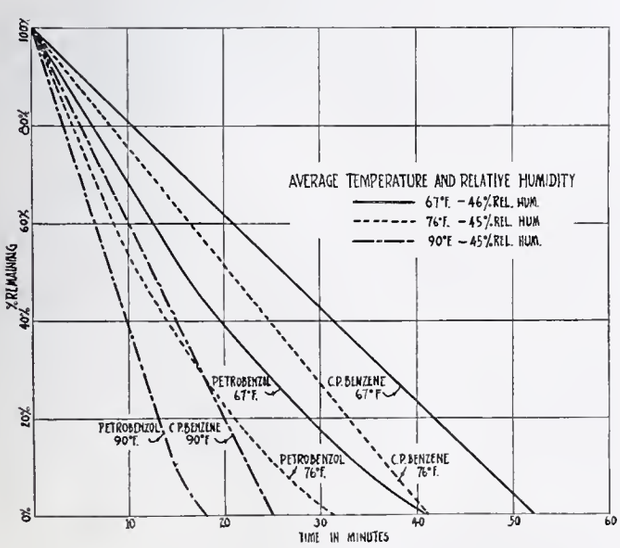

Figure 2. Evaporation Curve

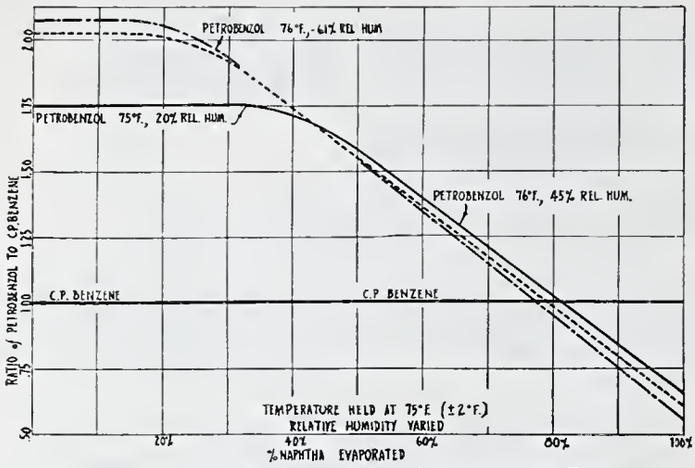

Figure 4. Ratio Chart of Evaporation Rates

The sensitiveness of this method necessitates precautions to eliminate drafts. It was found that the air disturbance caused by the opening of a door, or walking rapidly past the pans during the evaporation test was sufficient in some cases to affect the results. This error would cause a variation from the straight-line evaporation of a c. p. material.

Experimental. Petrobenzol (a petroleum naphtha which evaporates in about the same time as c. p. benzene) and c. p. benzene were evaporated under varying air conditions: temperatures of 90° F. (32° C.), 75° F. (24° C.), and 65° F. (18° C.), and relative humidities of 20, 45, and 60 per cent. Maximum temperature variation during the test was 2° F., and maximum relative humidity variation was 1.5 per cent. It was desired to determine whether c. p. benzene would evaporate in a straight-line curve under less ordinary conditions, and whether the difference of evaporation rate of the two solvents was constant as the air conditions were varied. From data gathered, Figures 2 and 3 were plotted.

Discussion of Results

Figures 2 and 3 show that by this method c. p. benzene gives a straight-line evaporation curve under the air conditions tried.

According to a method previously used (*2*) for comparing rates of evaporation, the difference in evaporation rate between Petrobenzol and c. p. benzene apparently remained constant under the conditions tried. Figures 4 and 5, derived from Figures 2 and 3, show the ratio of evaporation rates of Petrobenzol as compared to c. p. benzene. c. p. benzene, evaporating at a constant rate, was taken as a base line, points above and below the base line representing evaporation rates more and less rapid, respectively, than the benzene. The variation in the Petrobenzol evaporation rate curves is less than might be expected from experimental error. These charts indicate, therefore, that the difference in evaporation rate between Petrobenzol and c. p. benzene remained constant under the conditions of the experiment.

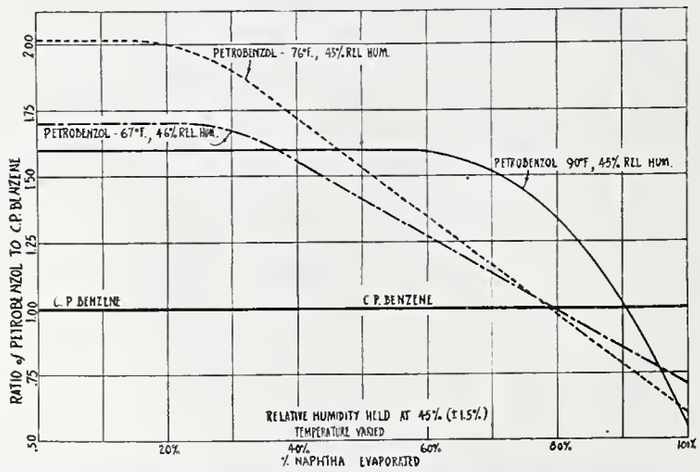

Figure 5. Ratio Chart of Evaporation Rates

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Acidity Titration of Low-Grade Rosins

During the years 1918 and 1920 there appeared in different well-known journals three communications from this laboratory fully describing a method by which the acidity (or alkalinity) of dark-colored solutions (or clear solutions viewed in artificial light) could be determined with the aid of a "pocket" spectroscope. The conditions of success were laid down for a number of different indicators and considerable detail for phenolphthalein. The method received at the time more publicity than the authors anticipated. Its general applicability having been shown, it was adopted here as routine procedure when necessary.

There has now appeared [Ind. Eng. Chem., Anal. Ed., **6**, 122 (1934)] a paper entitled "Acidity Titration of Low-Grade Rosins" by W. C. Smith, which describes the same spectroscopic titration as the new discovery of that author.

The only public result of private correspondence on the subject has been an obscure paragraph marked "Correction" [*Ibid.*, **6**, 192 (1934)]. Mr. Smith there mentions a paper [J. Ind. Eng. Chem., **12**, 274 (1920)] as being on "the acidity of red wines and fruit juices," though he was aware that half the publication, under a subheading, dealt with spectroscopic titration in general and with the use of phenolphthalein in this connection in particular, covering in itself all the ground of his own paper in every respect except as to its obvious utility in resin determinations.

Mr. Smith also failed to call attention to the fact that he had attributed to others a method of examination used and published by the late A. H. Allen.

I greatly regret having to make publicly, for my laboratory and for an eminent dead man, claims which should have been admitted at once.

From correspondence, however, there emerges the fact that C. Gautier and P. Coursaget published a paper, "Utilisation pour l'acidimétrie du spectre d'absorption de la matière colorée en rouge violacé que donne avec les alcalis la phénolphthaléine" [*Compt. rend. soc. biol.*, **81**, 733 (1918)] which in some respects anticipated the paper from this laboratory published in 1920, though following, in point of time, other articles from here [*J. Soc. Chem. Ind.*, **37**, 117T (1918) and *J. Am. Chem. Soc.*, **50**, 873 (1918)].

I have been unable to find any notice of this paper in the abstract journals published by the Chemical Society, the American Chemical Society, or the Society of Chemical Industry. I have no access to the original paper. I am therefore unable to tell how far the published results overlap. If they do so, I wish to offer to Messrs. Gautier and Coursaget the most full apologies. I am sure these gentlemen will realize that chemical workers in this laboratory could not be expected to study journals devoted to biology. It will also be realized that, as two publications on the subject had already appeared from here, we might reasonably be considered as having a prior right to continue the line of investigation as far as we saw fit. This right was exercised, though proper notice of other workers would certainly have been taken, had their publication been available.

Alfred Tingle

Customs-Excise Laboratory
Department of National Revenue
Ottawa, Canada. August, 1934

Micromethods for Determination of Zinc

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THE purpose of this paper is to describe methods for quantitatively estimating the small amounts of zinc which may be found in plant materials and other substances. These methods require ashing to remove organic material, then separation of the zinc from most other associated metallic ions. The ash is extracted with hydrochloric acid and the zinc separated by means of hydrogen sulfide or oxalic acid and ferrocyanide. The isolated zinc may be estimated by nephelometry, by iodometric titration, by a micromodification of the long-known ferrocyanide titration, or by the polarigraph (*5*). The amount of zinc to be measured may be 0.5 to 0.1 mg., quantities sometimes found in 5 grams of plant material. The polarigraph is capable of measuring very much smaller amounts.

The methods described in this paper present the following improvements: use of a convenient citrate buffer adjusted to pH 3; more accurate adjustment to desired pH; use of powdered talc as a filter aid; several turbidity standards; and considerable saving of the analyst's time. A description of the ferrocyanide-oxalate separation and details of the iodometric titration of minute amounts of zinc are also given.

The time required to make a single determination by the hydrogen sulfide separation and ferrocyanide turbidity method may be 2 to 3 hours. One analyst can complete ten to twenty determinations in 8 hours, depending on the character of the samples to be analyzed and the adequacy of laboratory equipment.

Before beginning an analysis, all the apparatus, chemicals, and water to be used should be tested for zinc. Jena and some other glassware easily give up zinc to dilute acid. Pyrex or Kavalier glassware seems satisfactory. Ordinary glass bottles and good porcelain seem to be free of soluble zinc. Most rubber stoppers and tubing give up zinc. In preparation and grinding of plant material, all copper, brass, bronze, or galvanized apparatus should be excluded. A nickel wire sieve and ordinary iron grinding mill may be used. Plant material should be pulverized to pass a 1-mm. sieve. Woody material, such as twigs of trees, may contain much more zinc in fine than in coarser portions, and therefore should be ground to pass a 1-mm. sieve and well mixed.

Analytical Procedure

The procedures of several chemists (*1, 3, 4, 7*) have been considered in working out this method. Most of the basic facts have long been known, but several new modifications of procedure have been introduced by the writer in order to simplify and shorten the work.

In Absence of Much Arsenic or Lead. In a 25-cc. porcelain evaporating or other appropriate dish, burn 1 to 5 grams of materials in a muffle at low red heat in order to avoid fusion of the ash. Apparently zinc is not lost at bright red heat, but more complete extraction of the zinc by dilute acid is secured and carbon is easier to burn off if the ash does not fuse.

To the ash from 5 grams of material, add about 15 cc. of water and 7 cc. of 3 *N* hydrochloric acid and set on the steam bath till about half the liquid has evaporated. Further concentration may cause gelatinization of silica so that filtration becomes difficult. So long as the silica remains in solution, it does not interfere in subsequent operations. Filter the extract into a 50- to 100-cc. conical flask and wash till the volume is 20 to 25 cc. In case there is little insoluble residue, filtration may be omitted. If much unburned carbon remains on the filter, ignite again, extract with acid, and add the extract to the main portion. Usually the insoluble ash contains very little zinc. (In one case, the ash from four filters was found to contain 0.005 mg. of zinc; in another, ash from 5 filters contained 0.015 mg. of zinc.)

Add a few drops of bromophenol blue indicator and ammonia until the solution becomes blue. Then add *N* hydrochloric acid until the solution is just yellow and the precipitate of iron, etc., is dissolved. Now add 3 to 5 cc. of sodium citrate buffer, according to amount of iron present. This buffer contains about 12 grams of sodium citrate and 23 grams of citric acid in 100 cc. and is adjusted to pH 3 by adding one or the other as needed. Its function is to maintain the proper pH, and to hold iron compounds in solution. A larger amount of citrate buffer does no harm. Set the flask on the steam bath till hot, then add dilute acid or ammonia till the solution is gray (neither yellow nor blue), with a pH of 3.0 to 3.4, and pass in a rapid stream of hydrogen sulfide for a minute or two. (When the solution contains much Fe^{+++}, it is difficult to adjust to pH 3 with bromophenol blue or other indicator. If the iron is previously reduced in slightly acid solution by the use of sulfur dioxide, from sodium sulfite or compressed sulfur dioxide gas, it is much easier to see the color change of the indicator.) If there is much precipitate of lead or copper, no filter aid is needed; if not much precipitate, add about 0.05 gram of acid-washed powdered talc (1 cc. of a 5 per cent water suspension), set the flask in cold water, and continue passing hydrogen sulfide slowly till cold. Cork the flask and set aside till ready to filter. The talc collects the zinc sulfide so that a clear filtrate may be obtained at once, but if desired, it may stand overnight before filtering. (Addition of copper to form cupric sulfide for flocculating the zinc sulfide has been recommended.)

Filter on a close-textured filter, such as Whatman No. 1, 7 cm. Wash with water saturated with hydrogen sulfide plus 5 cc. of 90 per cent formic acid per liter (*4*). Washing must be very thorough, five to six times after the original solution has all passed through, in order to remove all the iron from the filter. The filter now contains the zinc as zinc sulfide, with possibly some arsenious, cupric, or lead sulfide. Small quantities of these impurities may be disregarded, but if there is more than 1 to 2 mg. of arsenic or 10 of lead, these ions should be removed before precipitating the zinc. It is best to start with another portion of the material to which no buffer has been added.

In Presence of Much Arsenic or Lead. Add concentrated hydrochloric acid to make the solution 6 *N*. Saturate with hydrogen sulfide, cork the flask, and set it on the steam bath till hot. Remove by filtration the yellow arsenic sulfide that coagulates. Collect the filtrate in an evaporating dish and evaporate until nearly dry. No loss of zinc occurs by evaporation of hydrochloric acid solutions on the steam bath, and this is preferable to neutralizing the excess acid with an alkali. Return the solution to the small flask and make 0.25 *N*, preferably by titration, since indicators are not accurate enough in the region of pH 0.52.

Pass a rapid stream of hydrogen sulfide into the solution for a few minutes till it is saturated. Cork the flask and set on the steam bath till hot. The lead sulfide, at first flocculent, soon becomes granular and is easily filtered out. To obtain the zinc in the filtrate, neutralize the solution to pH 3, add citrate buffer, and precipitate the zinc with hydrogen sulfide as above described.

Attempts to remove the lead from the solution of the original ash by use of sulfuric acid instead of hydrochloric acid as solvent failed to retain the zinc in solution. Most of the lead was removed as lead sulfate, which seemed to retain some zinc.

In most cases, there is not enough lead to interfere or prevent complete separation of the zinc sulfide in such condition that it is easily soluble in *N* hydrochloric acid. Small amounts of lead, up to 10 mg., may be present with the zinc sulfide, yet from this the zinc may be extracted by cold *N* hydrochloric acid, which also dissolves some of the lead. By applying the acid in portions of 2 to 3 cc. at a time to the filter, the zinc is entirely dissolved by about 15 cc., nearly all in the first 5 cc. The solution of zinc, with perhaps some lead, is now ready for estimation of the amount of zinc, as described below.

There is danger of occluding some zinc sulfide with the

lead sulfide in separating the lead, unless the free acid is kept up to 0.25 N, and from this strength of acid not all the lead is usually removed by hydrogen sulfide.

A very little arsenic precipitated with the zinc sulfide may prevent solution of the latter in N hydrochloric acid, and therefore must be removed first. If the solution contains enough silica to interfere in filtration, it may hinder solution of the zinc sulfide and so should be removed by dehydration of the original acid extract of the ash.

Oxalate-Ferrocyanide Method. The success of this separation depends on the fact that the ferrocyanides of iron, lead, manganese, arsenic, and calcium are easily soluble in a 7 to 8 per cent solution of oxalic acid which also contains enough hydrochloric acid to make it about 0.5 N in free hydrochloric acid, while the ferrocyanides of zinc and copper are very insoluble in the same acid mixture. This unpublished method was devised by P. R. Stout in the attempt to find a way to estimate the zinc in such a complex mixture by means of the polarigraph.

Ash 2 grams of plant material as described above and extract the soluble material with about 3 cc. of 3 N hydrochloric acid and 10 cc. of water. After half the liquid has evaporated on the steam bath, add 10 to 11 cc. of a 10 per cent solution of oxalic acid. When further evaporation has reduced the total volume to about 20 cc., remove from the heat, and if copper is present, pass in hydrogen sulfide for a few minutes and let stand till cold, best overnight. Filter out the insoluble residue and the cupric sulfide, together with the oxalates of calcium and lead, and wash with a little 5 per cent oxalic acid. To the clear filtrate add 10 cc. of 10 per cent oxalic acid and 1 cc. of 4 per cent potassium ferrocyanide and mix. A white cloud indicates the presence of zinc. If no cloud appears, appreciable amounts of zinc are absent. After 10 to 15 minutes, filter out the zinc ferrocyanide. Addition of 0.02 gram of powdered talc aids in obtaining a clear filtrate. It may be necessary to return the filtrate to the filter once or twice in order to retain all the precipitate. Wash the filter twice with 5 per cent solution of oxalic acid, decompose the precipitate on the filter with 5 to 10 cc. of N sodium sulfide, and wash three times with some of the same solution diluted with three volumes of water. Lastly, wash once with water.

If zinc was present in the solution, zinc sulfide now remains on the filter. Dissolve the zinc off with N hydrochloric acid, returning the filtrate to the filter until it comes clear. In the clear filtrate, the zinc is again precipitated by potassium ferrocyanide and estimated nephelometrically, or it may be precipitated by hydrogen sulfide and estimated as described below.

If desired, centrifugalizing may be substituted for filtration in making oxalate separations.

In making these separations, the concentration of hydrochloric acid must be about 0.5 N, sufficient to prevent precipitation of calcium and lead oxalates, and the solution must be strong enough in oxalic acid, about two-thirds saturated, to prevent appearance of much blue due to ferric ion. If the mixture on the filter becomes blue, iron is likely to be present with the zinc in the final filtrate from which the iron may be removed by repeating the separation.

Although one inexperienced with this method may not succeed well at first, it is preferable to the hydrogen sulfide separation when there is much lead or arsenic in the solution.

Estimation of Zinc

Nephelometric Method. The zinc solution dissolved off the filter by N hydrochloric acid is collected in a 20-cc. flat-bottomed specimen tube suitable for comparisons in the manner in which a Nessler tube is used. To the zinc solution add 2 cc. of 5 M sodium hydroxide and fill to the mark with N hydrochloric acid. Add 2 drops of 2 per cent potassium ferrocyanide; mix quickly. After standing about 15 minutes to develop its greatest turbidity, it is compared with similar tubes containing known amounts of zinc precipitated in the same manner. For comparison, set the tubes on a dead black surface where the light strikes the tube perpendicular to its length. Tubes containing 0.02, 0.04, 0.06, 0.08, and 0.10 mg. of zinc will usually be sufficient and permit a better estimation of the amount than if a single tube is used to contain the standard which is adjusted to match the unknown by pouring out part of the mixture. The standards are good for an hour or so, but should be made fresh for each set of samples to be examined.

The cloudy suspension of zinc ferrocyanide should be pure white, not colored blue by iron, and the precipitate should not settle perceptibly in 1 hour. Use of a nephelometer to measure the turbidity may promote increased accuracy. Greater precision is attainable by use of a photoelectric cell in making the comparisons. If some lead sulfide was mixed with the zinc sulfide on the filter, some of the lead goes with the zinc dissolved by the N hydrochloric acid, but this does no harm since lead ferrocyanide is easily soluble in 0.5 N hydrochloric and seems not to influence the turbidity produced by the zinc. In order to secure greatest accuracy, concentrations of reagents, manner of mixing, and all other conditions in standards and in unknowns should be as nearly alike as possible. Iron, copper, and manganese must not be present. Not more than 0.1 mg. of zinc in 20 cc. of solution is well measured by this method.

Measurement by Polarigraph. This instrument permits measuring to ± 5 to 10 per cent accuracy much smaller amounts of zinc than can be measured by chemical methods. However, the apparatus is expensive and not readily available, and the necessary special preparation of the solution is not generally understood.

Iodometric Titration Method. This method, a modification of that proposed by Lang (*6*), is adapted to measuring with a good degree of accuracy 0.05 to 1.0 mg. of zinc or more.

The reagents needed are:

1. A phosphate buffer made by mixing 25 grams of acid potassium phosphate with 5 cc. of sirupy phosphoric acid and diluting to 100 cc. The pH is adjusted to 3 by addition of acid or alkali as needed. For use, it is diluted 10 times.
2. Potassium iodide, 20 per cent solution in water.
3. Clear starch for indicator, 0.5 per cent in water.
4. Potassium ferricyanide, 1 per cent in water, made fresh every few days.
5. Sodium thiosulfate, 0.001 N in cold, boiled water, made fresh every day by dilution of a 0.01 N solution. It loses strength perceptibly in a few hours.

Titration Procedure

The zinc chloride from the zinc sulfide dissolved off the filter by N hydrochloric acid is collected in a 50-cc. porcelain casserole and evaporated to dryness on the steam bath. To the dry residue, add, in the order given, 0.5 cc. of dilute phosphate buffer, 1 to 2 drops of potassium iodide, 3 drops of starch, and 3 drops of potassium ferricyanide. If zinc is present, the mixture becomes blue and is titrated with sodium thiosulfate slowly till the blue color changes to pure yellow. After a few minutes, the blue returns slowly, but this is disregarded. If no zinc is present some blue appears, but this may be discharged by 1 or 2 drops of sodium thiosulfate, 1 cc. of which usually represents about 0.1 mg. of zinc. It should always be checked against a known amount of zinc at the time the unknown is titrated. It is hardly worth while to prepare for making this titration unless a number of samples are to be analyzed at one time.

Two reactions are apparently involved in this titration:

$$K_3Fe(CN)_6 + KI \leftrightarrows K_4Fe(CN)_6 + \tfrac{1}{2}I_2 \qquad (1)$$

This is slow and reversible and soon reaches equilibrium, but if zinc is present the second reaction takes place, so that iodine is set free as long as any zinc remains.

$$Zn^{++} + K_4Fe(CN)_6 = ZnK_2Fe(CN)_6 + 2K^+ \qquad (2)$$

This is practically instantaneous.

Lang indicates that the reaction is

$$2K_3Fe(CN)_6 + 2KI + 3ZnSO_4 = K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4 + I_2 \qquad (3)$$

The ferricyanide and iodide of Reaction 1 also react slowly to liberate free iodine by action of the oxygen of the air, so that oxygen should be excluded as much as possible. To this end, the titration is performed in a very small volume and mixing is obtained by gentle rolling of the casserole from side to side

without use of a stirring rod or other means of vigorous agitation. If the liquid is covered with a layer of gasoline or the work is done in an atmosphere of carbon dioxide, the return of the blue color after completion of the titration is very much slower, supposedly because oxygen is nearly excluded. However, since a titration may be completed within less than a minute, there is very little error from the oxygen of the air. Copper, iron, and manganese must be absent.

Estimation of the separated zinc by the colorimetric phosphate method (*7*) was not successful because of difficulty in removing all phosphate not combined with zinc—i. e., a sufficient amount of phosphate to vitiate the determination was always found in running a blank on reagents.

The well-known method for macrotitration of zinc with ferrocyanide and uranium indicator may be used when the amount of zinc is more than 0.3 mg., though the iodometric method above described is probably preferable, being quicker and better adapted to measurement of very small amounts.

The Eegriwe test for zinc (*2*) with diethylaniline and potassium ferricyanide is not much more sensitive than the cloud test with potassium ferrocyanide and is not adapted to quantitative estimation of zinc.

Results Obtained

Zinc Estimated by Turbidity. To the solution of the ash of several 5-gram portions of peach leaves 20 mg. of lead as acetate were added, and the zinc was separated by hydrogen sulfide and estimated by ferrocyanide turbidity as above described.

Without added lead, the zinc found on two tests was 0.15 mg. each time. With 20 mg. of lead added, the zinc found was 0.16 mg. in each of six tests. With reagents alone plus 20 mg. of lead, the zinc found was 0.03 mg., indicating a plus error of 0.02 mg. of zinc, due to added lead, which is almost within the limits of error of reading the turbidities.

To 5-gram portions of pine sawdust were added varying amounts of zinc, the material was burned, and zinc estimated:

Zinc Added	Zinc Found
Mg.	*Mg.*
0.	0.06
0.02	0.08, 0.08
0.05	0.12, 0.12
0.10	0.15, 0.16

Zinc Estimated by Iodometric Titration. To 5-gram samples of apple leaves containing much lead varying amounts of zinc were added. The mixtures were burned, the zinc was separated, and the amount measured by iodometric titration:

Zinc Added	Zinc Found
Mg.	*Mg.*
0.	0.015, 0.015, 0.015
0.05	0.055
0.20	0.26, 0.22

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Quantitative Determination of Lead as Periodate

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In another paper (*3*) the proper conditions have been given for the precipitation of lead as pure triplumbic paraperiodate. It was found that this salt was sufficiently insoluble in very dilute acid solutions to make possible its use in the volumetric and gravimetric determination of lead.

Experimental

Weighed samples of Mallinckrodt's reagent-quality lead or Kahlbaum's sheet lead were dissolved in nitric acid and evaporated to dryness. The dry salt was then dissolved in 200 cc. of 0.025 *N* nitric acid and the lead precipitated at 100° C. by the slow addition of 2 grams of sodium periodate, $NaIO_4$, dissolved in 50 cc. of water. When the amount of lead was very small, no precipitate formed until after 1 cc. of the periodate solution had been added. When this occurred, it was necessary to decrease the acidity to 0.006 *N;* otherwise the precipitate did not have the theoretical composition. After the periodate was added, the solution was cooled in ice water and the cold solution stirred for 0.5 hour, because supersaturation was very pronounced. The lead periodate was filtered on a porcelain filtering crucible, washed with ice water, and dried for 2 hours at 110° C. It was then weighed as $Pb_3H_4(IO_6)_2$. Results of analyses are shown in Table I.

To determine the lead periodate volumetrically the method of Andrews (*1, 2*) was used, because the best solvent for the salt is concentrated hydrochloric acid. The equation for the reaction can be expressed as follows:

$$Pb_3H_4(IO_6)_2 + 8HCl + 6H_3AsO_3 = 3PbCl_2 + 2ICl + 6H_3AsO_4 + 6H_2O$$

If arsenious acid is present in excess, all the chlorine will react with it to form arsenic acid. The excess arsenious acid can then be titrated with iodate, using chloroform as indicator.

Table I. Gravimetric Determination of Lead as $Pb_3H_4(IO_6)_2$

Lead Taken	Lead Found	Error
Gram	*Gram*	*Mg.*
0.7001	0.7001	±0.0
0.6953	0.6954	+0.1
0.6028	0.6025	−0.3
0.5596	0.5596	±0.0
0.5591	0.5588	−0.3
0.5553	0.5552	−0.1
0.3853	0.3852	−0.1
0.1145	0.1147	+0.2
0.1121	0.1122	+0.1
0.0735	0.0734	−0.1

Table II. Volumetric Determination of Lead as $Pb_3H_4(IO_6)_2$

Lead Taken	Lead Found	Error	As_2O_3 Added
Gram	*Gram*	*Mg.*	*Gram*
0.5920	0.5921	+0.1	0.7111
0.4896	0.4895	−0.1	0.7447
0.3069	0.3067	−0.2	0.4006
0.2920	0.2920	0.0	0.4135
0.2060	0.2063	+0.3	0.3297
0.1554	0.1557	+0.3	0.2320
0.1103	0.1101	−0.2	0.1299
0.1037	0.1035	−0.2	0.1271
0.1001	0.0999	−0.2	0.1125
0.0653	0.0655	+0.2	0.1003
0.0496	0.0494	−0.2	0.2116

The precipitate was filtered into a Gooch crucible, the bottom of which was covered with a filter-paper disk, washed thoroughly, and transferred to a 150-cc. conical flask. An excess of arsenious oxide previously dissolved in a concentrated solution of sodium hydroxide or a suitable volume of standard arsenite solution was added to the flask. Concentrated hydrochloric acid was slowly added to the cold solution, the flask being agitated until all the lead periodate dissolved, which required 35 to 40 cc., and the solution was titrated with 0.1 *N* potassium iodate until it was a light brown in color. A little chloroform was then added and the titration completed. The results of the volumetric determination of lead as periodate are shown in Table II.

Separation of Lead as Periodate from Other Metals

The possibility of separating lead as $Pb_3H_4(IO_6)_2$ from other metals is rather limited, since most metals form periodates which are insoluble in low acid concentrations. The results of the separation of lead as periodate from other metals are shown in Table III. The lead was determined volumetrically.

Summary

Lead can be separated from nickel, copper, zinc, cadmium, aluminum, calcium, and magnesium by precipitating it as $Pb_3H_4(IO_6)_2$ from 0.025 *N* nitric acid solution by the addition of sodium periodate. The precipitate can be weighed or determined volumetrically by dissolving it in concentrated hydrochloric acid containing an excess of standard arsenite, and titrating the excess with standard iodate, using chloroform as indicator.

Table III. Separation of Lead as $Pb_3H_4(IO_6)_2$

Lead Taken	Lead Found	Error	Other Metals Present
Gram	*Gram*	*Mg.*	*Gram*
0.6771	0.6778	+0.7	0.4 Ni
0.5643	0.5709	+6.6	0.26 Cu[a]
0.5163	0.5160	−0.3	0.05 Cu
0.5375	0.5374	−0.1	0.21 Al
0.5161	0.5163	+0.2	0.22 Zn
0.5944	0.5971	+2.7	0.37 Cd[a]
0.5570	0.5575	+0.5	0.07 Cd
0.5438	0.5440	+0.2	0.2 Ca
0.5567	0.5563	−0.4	0.2 Mg

[a] Double precipitation would obviously have been satisfactory.

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Electrometric Determination of Chlorides in the Ash and Sap of Plants and in Ground Waters

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Best (*2*) has described the use of a silver–silver chloride electrode for the titration of chloride ions in a suspension of soil and water. He reported that the method was sensitive to within one drop of a 0.028 *N* silver nitrate solution and that it was applicable for various types of soils.

After being used for several years with entire satisfaction for both mineral and organic soils, the method was adapted to determine chlorides in the ash of plants and in the expressed saps. In those cases where it can be employed the method is particularly desirable for direct use upon liquid plant sap, where the presence of coloring matter generally prohibits the use of a color indicator. Furthermore, it permits a measurement of the actual chloride-ion content of the unaltered sap.

This paper deals with comparative analyses of the chlorine content of plants and of their saps by the electrometric method and by the standard method (*1*) in which chlorides are determined in an acid extract of the ash of the material, and discusses the limitations relative to the direct estimation of chlorides in liquid saps and juices.

Electrometric Method

Briefly, the electrometric titration of chloride ions is based upon the change in polarity of a silver–silver chloride electrode when the chloride-ion concentration of the liquid in which it is immersed reaches a minimum when titrated with a solution of silver nitrate. The method requires the use of a reference electrode of the same potential—0.521 volt at 25° C.—as that of the silver–silver chloride electrode at the point where it changes in polarity. This reference electrode consists of a platinum wire dipping in a solution of pH 3.1 to 3.3 made up according to the method of Clark (*3*) with the substitution of sulfuric for hydrochloric acid. Enough quinhydrone is added to saturate the solution.

The silver–silver chloride electrode is prepared by coating 3 to 5 cm. of a silver wire with silver chloride by electrolysis in a sodium chloride solution about 0.1 *N*. The current from a partially exhausted dry-cell battery is sufficient and the rate of deposition may be partially controlled by dilution of the sodium chloride solution. The coating should be thick enough to produce a light brown color on the wire and should be deposited slowly enough to extend over a period of 15 to 30 minutes. If wire about 0.8 mm. in diameter is used it is sufficiently rigid to be carried directly to the binding post of the galvanometer. Electrodes prepared in this way have retained their sensitivity for months if stored in the dark when not in use, with the silver chloride coated tips immersed in distilled water.

Best made this system suitable for the determination of chloride ions in solutions of varied reactions and buffer capacities by connecting the two electrodes by means of a potassium nitrate bridge, made by filling a glass U-tube with a heated mixture consisting of 5 per cent of purified agar agar in a saturated solution of potassium nitrate.

A galvanometer of a sensitivity of 0.125 microampere per millimeter was used for most of the measurements, although one of 0.5-microampere sensitivity will do very well.

Effects of Acids, Salts, and Bases

In order to ascertain the feasibility of the use of the electrometric method for chlorides in the acid extracts of ashed

samples, a study was made of the effects of the presence of acids, salts, and bases upon results obtained with a standardized solution of sodium chloride. It was found that the method was applicable in the presence of appreciable amounts of sodium nitrate and of sodium sulfate. The end point was unaffected by either nitric or sulfuric acid in concentrations as high as 0.2 *N*. Neither sodium nor ammonium hydroxide could be present even in traces. Normal concentrations of either citric or tartaric acids, or of their salts, caused no interference in these trials with pure sodium chloride solutions.

Chlorides could be accurately determined in the standard sodium chloride solution, made distinctly alkaline with sodium hydroxide, if brought back to the acid side with 0.2 *N* sulfuric acid, using methyl red as an indicator. Since a considerable excess of the 0.2 *N* sulfuric acid makes no difference, the neutralization can be quickly accomplished. These findings were similar to those recently published by Snyder (*4*), who adjusted his soil solutions to a pH of 2 as indicated by thymol blue test paper, and form a basis for the use of the electrometric method to determine chlorides in ashed samples of plant materials. A blank should be run on all reagents to make sure that they are free from chlorides.

Electrometric Method with Ashed Samples

By neutralizing the nitric acid extracts of the ashed saps of plants with sodium hydroxide, then making acid again with 0.2 *N* sulfuric acid in the manner described above, the data tabulated in Table I were obtained. Comparable analyses are in close agreement for widely different types of saps except the sap of the leaves of the grapefruit and the juice of its fruit. In both cases the chloride contents were so low that the volumetric titration end point was not sufficiently sensitive. Besides its extreme sensitivity the electrometric method is considerably more convenient, as the precipitation and filtration steps of the volumetric method are eliminated.

Table I. Determination of Chlorides in Ashed and Liquid Plant Saps

Source Materials	Ashed Saps: Volumetric	Ashed Saps: Electrometric	Ashed Saps: Variation from volumetric		Liquid Saps: Electrometric	Liquid Saps: Variation from volumetric of ashed saps	
	P. p. m.	*P. p. m.*	*P. p. m.*	%	*P. p. m.*	*P. p. m.*	%
Para grass leaves	2335	2292	−57	2.44	2436	+101	4.33
Para grass[a] leaves plus sodium chloride	2335	2307	−28	1.20	2472	+137	5.87
Sugar cane stems	519	512	− 7	1.35	523	+ 4	0.77
Grapefruit leaves	96	109	+13	13.54	180	+ 84	87.50
Grapefruit	45	47	+ 2	4.45	115	+ 70	155.56

[a] After deducting for the added sodium chloride.

Samples of the seeds and pods of peas and beans and of grass clippings were ashed in the presence of sodium carbonate and then analyzed for total chlorine by the volumetric and electrometric methods. Table II shows that the two methods are in close agreement except in the samples that were lowest in chlorine content. Because of its greater sensitivity the electrometric titration is probably the more correct in those cases.

Table II. Total Chlorine in Plant Material

(Oven-dry basis)

	Peas, Green Seeds	Peas, Green Pods	Beans, Green Seeds and pods	Grass Clippings
	%	%	%	%
Sample 1:				
Electrometric	0.076	0.110	0.198	0.301
Volumetric	0.085	0.118	0.185	0.300
Per cent variation from volumetric	10.59	6.78	7.03	0.33
Sample 2:				
Electrometric	0.116	0.364	0.210	..
Volumetric	0.114	0.369	0.207	..
Per cent variation from volumetric	1.76	1.36	1.45	..

Results with Liquid Saps

It may be noted in Table I that the chloride-ion values given by the electrometric titration of the unaltered sap of grass leaves and of sugar-cane stems are 4.33 and 0.77 per cent higher, respectively, than those obtained volumetrically on ashed portions. Parallel determinations on grass-leaf sap to which a known amount of sodium chloride was added gave a 5.87 per cent increase after deducting for the added chlorine. These findings indicate that the slightly higher results obtained by the direct titration of the grass sap were due partly to a loss of chlorides in ashing but mostly to some inherent property of the sap. Direct titrations of the sap of grapefruit leaves and of the juice of grapefruit were very much greater, especially in the latter case. In the same way the end point drifted in the positive direction (requiring more silver nitrate) in these two cases and particularly with the grapefruit juice.

Grapefruit juice is known to contain rather large amounts of the salts of citric acid. The hydrolysis of these citrates might have caused the positive drift in the end point just as it was caused by traces of free sodium ions in the standard sodium chloride solutions discussed above. The fact that neither sodium citrate nor sodium tartrate affects the end points in the pure sodium chloride solutions, whereas they are presumed to be the cause of the positive drift in the grapefruit juice, may be due to an increased hydrolysis of these weak acid salts in the presence of the colloidal material of the juice. The juice darkened rapidly after adding silver nitrate. So far as could be observed in the grass and sugar-cane saps this darkening did not take place. The titration end points did not drift with these.

The direct sap titration of the sugar-cane stem sap varied only 0.77 per cent (Table I) from the volumetric titration after ashing. This sap contained more solids in true but less in colloidal solution than the other saps. Trials with the standard sodium chloride solution showed that large amounts of sugars in solution did not interfere with the titration.

It appears, then, that the direct electrometric titration upon the saps of plants or the juices of fruits may be too high if much colloidal material is present. When appreciable amounts of the salts of weak acids are also present the chlorine content cannot be determined without first ashing the material. In the case of many saps, however, chlorides may be determined directly and conveniently in the unaltered sap with a fair degree of accuracy. The only way to ascertain the accuracy for a given type of sap is to run a test analysis by ashing. If the end point drifts appreciably it may be inferred at once that ashing is necessary.

Table III. Chloride Contents of Ground Waters

Sample	Electrometric	Volumetric	Variation from Volumetric	
	P. p. m.	*P. p. m.*	*P. p. m.*	%
1	1561	1642	81	4.93
2	676	691	15	2.17
3	147	149	2	1.34
4	93	96	3	3.13

Ground Waters

The volumetric and electrometric titrations for chlorides in various samples of ground waters checked well with each other (Table III). Samples 1 and 2 were obtained from limestone strata and carried considerable amounts of sulfates. When freshly exposed, there was enough hydrogen sulfide in sample 1 to be detectable by its odor. There is no particular advantage in using the electrometric method where a volumetric titration with a potassium chromate indicator can be employed, as neither method requires any intermediate manipulation or precipitation. When the chloride content

of the water or of a water extract is very low, however, the electrometric titration is preferable as it is considerably more sensitive.

Summary

Comparative analyses of the chlorides of the leaf and stem saps of plants were made electrometrically and volumetrically after ashing and by an electrometric titration of the unaltered saps. The two methods are in close agreement when used upon the acid extracts of plant materials or of their saps. The electrometric titration of chlorides in such acid extracts is preferred to the volumetric method because it is time-saving and because of its greater sensitivity.

Chlorides in the saps of some plants can be titrated directly by the electrometric method. The ashing step must be included in juices, such as those of citrus fruits, that contain appreciable amounts of the salts of weak acids.

The electrometric titration of chlorides in ground waters, which contained traces of sulfides and appreciable amounts of sulfates, checked closely with the chromate volumetric method and had a more sensitive end point.

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Determination of Tellurium in Tellurium Lead and Tellurium Antimonial Lead

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Although lead has been known since the earliest times, it is today one of the most useful of metals, finding extensive application as cable sheathing, water pipes and drains, tank linings, and heating coils. Hence, any treatment, whether physical or chemical, that improves the physical properties of lead is rendering industry a real service. The properties (*12*) that commend lead are its pliability and resistance to corrosion. Metallurgists have long known that small amounts of another metal may increase the hardness and tensile strength of lead. A lead containing a maximum of 0.08 per cent of copper and sold to the trade as "chemical lead" is harder, has more tensile strength, and is believed by many users to be more resistant to corrosion than pure lead. Singleton and Jones (*18*) claim that tellurium not only increases the tensile strength of lead and antimonial lead to a greater extent than copper does but also increases its resistance to corrosion. Tellurium lead and tellurium antimonial lead, each containing not less than 0.06 per cent nor more than 0.08 per cent of tellurium, are now marketable products, the patent rights for their manufacture in the United States being held by the National Lead Company.

The introduction of tellurium lead and tellurium antimonial lead creates an unusual problem for the analyst—the exact estimation of small amounts of tellurium in these products. Tel urium is regarded as a rare element. Textbooks on analytical chemistry allot little or no space to its consideration, and the chemist in most commercial laboratories seldom has occasion to make a determination. Indeed, he rarely in the course of his work considers it as an interfering element. Low consumption and restricted output, no doubt, have contributed to this general opinion.

Volumetric methods of determination have been developed depending upon the reduction of telluric acid (H_2TeO_4) to tellurous acid (H_2TeO_3), and conversely the oxidation of tellurous acid to telluric acid. Gooch (*8*) makes the reduction with potassium bromide in a sulfuric acid solution, while Browning (*2*) uses strong hydrochloric acid. The liberated bromine in the one case and the liberated chlorine in the other are passed into a solution of potassium iodide, the iodine set free being titrated with sodium thiosulfate. Gooch (*7*) oxidizes tellurous acid with a measured excess of potassium permanganate and titrates the excess with oxalic acid. Tellurous acid may also be determined by a volumetric precipitation method using potassium iodide as the precipitant, the end point being reached when no precipitation of tellurous iodide takes place upon further addition of the potassium iodide (*10*). Evans (*6*) reduces tellurium to the elemental form and then dissolves it in sulfuric acid in the presence of a measured excess of iodine solution and titrates back with standard arsenite solution. Tellurium may be determined gravimetrically by reduction to elemental tellurium, by conversion to the sulfate (*1*), as tellurium dioxide (*3*), and by the treatment of tellurous acid with potassium iodide in the presence of hydrochloric acid and a weighed amount of finely divided silver, whereby tellurium is precipitated and the liberated iodine is absorbed by the silver. From the increased weight of the insoluble material the tellurium may be calculated (*17*). Tellurium may also be determined electrolytically (*19*).

Tellurium is generally determined gravimetrically as elemental tellurium. There are a number of reducing agents used to make the precipitation, the most common being sulfur dioxide, sodium sulfite, stannous chloride, titanium trichloride, hypophosphorous acid, hydrazine hydrochloride and several of the metals in acid solutions, and grape sugar, hydroxylamine hydrochloride, and hydrazine hydrochloride in alkaline solution. (Brukl and Maxymowicz make a reduction with sodium sulfite in an alkaline solution, *4*). Lenher and Homberger (*14*) use both sulfur dioxide and hydrazine hydrochloride to make the reduction. MacIvor (*15*) discusses the merits of several of the reducing agents alone and in combination and points out that the amorphous precipitate of tellurium oxidizes when exposed to the air. For this reason Gooch (*9*) prefers to weigh tellurium as tellurium dioxide. Clauder (*5*) finds that oxidation of amorphous tellurium takes place, but states the difficulty may be overcome by precipitating the tellurium in a crystalline form by proper control of conditions. Treadwell (*20*) claims that tellurium thrown down with sulfur dioxide will not oxidize to any appreciable extent during the drying of the precipitate at 105° C.

In an attempt to work out a method for the determination of tellurium in pig lead the method of Lenher (*13*) was chosen as a starting point. Lenher effects solution with nitric acid and removes the bulk of the lead with sulfuric acid and the remainder by evaporating to fumes. The tellurium is then precipitated as a disulfide, dissolved in sodium sulfide, reprecipitated with sulfuric acid with the aid of hydrogen sulfide, dissolved in nitric and sulfuric acids, again taken to fumes, again precipitated as a disulfide, dissolved in hydrochloric acid and potassium chlorate, and finally thrown down with sulfur dioxide and weighed.

The experience of this laboratory with hundreds of analyses of commercial leads has shown that bismuth in ordinary lead and copper in chemical lead are the only impurities present in sufficient amount to interfere to any appreciable extent. In removing them by means of the alkali sulfide separation the author found that a small amount of tellurium due to the dissociation of tellurium disulfide (*16*) remained behind with

the bismuth or copper residue, the amount depending upon the temperature of the solution and the duration of the digestion, and that this small amount could be recovered without contamination by either bismuth or copper. The procedure in testing for tellurium was to dissolve weighed amounts of tellurium, copper, and bismuth in nitric acid and make the separate solutions up to a definite volume. Measured volumes were then added to a weighed portion of a very pure lead prepared by this laboratory. A description of the method in detail and the results obtained (Table I) are given below.

Determining Tellurium in Tellurium Lead

Weigh 12.5 grams of the lead sawings into a 500-cc. graduated flask, add a measured volume of the tellurium solution and a measured volume of the copper or bismuth solution, and then add 100 cc. of nitric acid (1 to 4). Heat on a water bath until solution is complete. Cool somewhat, add 25 cc. of sulfuric acid (1 to 1), cool to room temperature, make up to the mark with water at room temperature, and mix. Filter 400 cc. of solution through a dry paper (discarding the first 20 cc. of filtrate) into a 600-cc. beaker and evaporate to fumes of sulfur trioxide. Cool, dilute to a volume of 50 cc. with water, add 5 grams of tartaric acid, and bring to boiling. Cool, allow to stand for 2 hours, filter, and wash. Discard the residue.

Through the filtrate pass hydrogen sulfide, filter, and wash with hydrogen sulfide water. Wash the precipitate back into the original beaker with as little water as possible, add a gram or two of sodium bicarbonate and 5 cc. of a 10 per cent solution of sodium sulfide, and digest in a warm place. Filter and wash. Reserve the residue.

Make the filtrate slightly acid with dilute sulfuric acid and again pass in hydrogen sulfide. Filter and wash as before. Wash the residue back into the original beaker with as little water as possible, add an equal volume of hydrochloric acid (sp. gr. 1.19) and about a gram of potassium chlorate, and bring to boiling. Filter through the same paper as before and wash several times with hot water. Gently heat to expel free chlorine, add a few cubic centimeters of nitric acid (sp. gr. 1.42), and evaporate to dryness on the water bath (*11*). Take up with 100 cc. of hydrochloric acid (9 to 1), add a gram or two of tartaric acid, just bring to boiling, pass in sulfur dioxide for 15 minutes, add 100 cc. of boiling water, and continue in passing in sulfur dioxide for 30 minutes. Allow to stand in a warm place 1 hour, again pass in sulfur dioxide for 20 minutes, filter through a prepared Gooch crucible, and wash several times with hot water. Do not allow the pad to become dry between washings. Finally wash once with 95 per cent grain alcohol, dry at 100° C. for 1 hour, cool, and weigh as elemental tellurium.

Treat the residue held in reserve with hot hydrochloric acid to which potassium chlorate has been added, and proceed as described above. The final precipitate of tellurium may be filtered separately or combined with the main portion.

In Table I the tellurium in the residue and that found in the main portion were filtered separately. The first three columns represent amounts added that should be present in the aliquot portions.

Table I. Determination of Tellurium in Lead

Tellurium Taken	Copper Added	Bismuth Added	Tellurium Found In residue	Tellurium Found In main portion	Error
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0100	....	....	0.0005	0.0096	+0.0001
0.0100	....	....	0.0006	0.0096	+0.0002
0.0100	....	....	0.0005	0.0094	−0.0001
0.0100	....	....	0.0004	0.0097	+0.0001
0.0100	0.0050	....	0.0025	0.0075	0.0000
0.0100	0.0050	....	0.0034	0.0069	+0.0003
0.0060	0.0050	....	[a]	0.0060	0.0000
0.0060	0.0050	....	[a]	0.0062	+0.0002
0.0100	....	0.0150	0.0012	0.0090	+0.0002
0.0100	....	0.0150	0.0010	0.0093	+0.0003

[a] Tellurium in the residue combined with that in main portion.

This method is not adaptable for the determination of tellurium in antimonial lead. Nitric acid is not a suitable solvent for antimony alloys nor is hydrochloric acid an efficient solvent for lead alloys. The prospect of effecting decomposition of 10 grams of material with boiling concentrated sulfuric acid did not seem to hold much promise of success. The common practice of bringing alloys of antimony and lead into solution is to employ mixed acids—either hydrochloric and nitric or nitric and tartaric acids. The former mixture was used in the method given below. The method is applicable for 6, 8, and 10 per cent antimonial lead. The results obtained are shown in Table II.

Determining Tellurium in Antimonial Lead

Weigh 10 grams of the sawings into a 250-cc. beaker and add about 175 cc. of bearing metal solution. [Bearing metal solution is prepared by dissolving 40 grams of potassium chloride in 1000 cc. of water, adding 400 cc. of hydrochloric acid (sp. gr. 1.19) and 200 cc. of nitric acid (sp. gr. 1.42), and mixing.] Heat until lead chloride begins to crystallize out and then decant the solution into a 400-cc. beaker. Again add 175 cc. of bearing metal solution and heat to complete solution of the alloy. Allow both portions to stand in the cold overnight and filter through the same paper into a 600-cc. beaker. Wash with cold hydrochloric acid (1 to 1). Discard the residue.

Evaporate the filtrate to dryness on a water bath, take up with 100 cc. of hydrochloric acid (9 to 1), just bring to boiling, pass in sulfur dioxide for 30 minutes, add 100 cc. of boiling water, and continue passing in sulfur dioxide for 30 minutes. Allow to stand in a warm place an hour and again pass in sulfur dioxide for 20 minutes. Filter through a Gooch crucible and wash a few times with hydrochloric acid (1 to 2); finally wash a few times with water.

Detach the asbestos pad, transfer both pad and crucible to a small beaker, add 10 cc. of nitric acid (sp. gr. 1.42) and 10 cc. of sulfuric acid (sp. gr. 1.84), warm until the tellurium precipitate is completely dissolved, cool, remove and wash the crucible, filter, and wash. Evaporate the filtrate to fumes of sulfur trioxide, cool, dilute to a volume of 50 cc., add 5 grams of tartaric acid, and bring to boiling. Cool, allow to stand an hour or so, and filter and wash if a precipitate has formed. Discard the residue.

Through the filtrate pass hydrogen sulfide and proceed exactly as in the determination of tellurium in lead.

In Table II are shown the amounts of copper, bismuth, and tellurium added to pure lead (samples I to IV). Samples V and VI are antimonial lead to which tellurium alone has been added.

Table II. Determination of Tellurium in Antimonial Lead

Sample	Tellurium Taken	Copper Added	Bismuth Added	Tellurium Found In residue	Tellurium Found In main portion	Error
	Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
I	0.0100	0.0050	....	0.0014	0.0085	−0.0001
II	0.0100	0.0050	....	0.0013	0.0084	−0.0003
III	0.0100	....	0.0050	0.0012	0.0085	−0.0003
IV	0.0100	....	0.0050	0.0010	0.0086	−0.0004
V	0.0100	....	....	0.0005	0.0094	−0.0001
VI	0.0100	....	....	0.0004	0.0093	−0.0003

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Metallic Silver as an Ultimate Standard in Volumetric Analysis

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This paper presents a precision method for the use of pure silver in standardizing a hydrochloric acid solution, a method for preparing silver for use as a standard in acidimetry, an analytical method for using silver as an ultimate standard in acidimetry, and a comparison of the analytical method with the precision method.

THE ease with which silver of a high degree of purity can be prepared, its stability even if given no more protection than a stoppered bottle, and its chemical behavior toward other elements, render it one of the most important standard substances in precision chemical measurements; and it is obvious that these characteristics should render it an ideal ultimate standard in volumetric analysis if a simple and accurate method were at hand for using it in this way. To provide such a method has been the object of this investigation.

Specifically, a scheme has been developed for standardizing a hydrochloric acid solution by determining the weight (or volume) of the acid solution which is equivalent to a known weight of pure silver. The procedure consists in dissolving a weighed portion of silver in nitric acid and then finding by a Gay-Lussac titration the weight (or volume) of hydrochloric acid solution which is just equivalent to the silver. Equivalence is assumed when two portions of the supernatant liquid above the precipitated silver chloride give equal opalescence on treating one with an excess of silver and the other with an excess of chloride. The precipitated silver chloride is not filtered or handled in any way.

The plan of the investigation was, first to prepare material of "atomic weight" purity and then by "atomic weight" measurements and manipulation to determine the ratio between a hydrochloric acid solution and metallic silver. This furnished a standard by which the results of the second part of the investigation could be judged—namely, proposed analytical procedures for the use of silver in standardizing the acid.

Preparation of Materials

The materials fall into two classes: "atomic weight" silver and reagents used in the precision measurements, and "analytical" silver and reagents used in the "analytical" measurements. In the preparation of the "atomic weight" silver and reagents the methods of Richards and his students (*5*) were followed, including double and sometimes triple precipitations, both chemically and electrolytically, washing with centrifugal drainage, and final fusing on pure lime in an atmosphere of pure hydrogen. The manipulation employed was also that of modern atomic weight workers—for example, the use of the Richards bottling apparatus (*6*).

"Analytical Silver." Two samples of analytical silver (A and B, Tables III and IV) were prepared as follows: Ordinary silver nitrate was recrystallized once from a saturated solution by the addition of concentrated nitric acid. These crystals were centrifugalized and dissolved in water, and the silver was precipitated hot with ammonium formate made by passing ammonia into freshly distilled formic acid. This silver was then washed and melted in portions in a lime-lined porcelain crucible. The lime lining consisted of four parts of analytical reagent calcium carbonate to one part of powdered calcium nitrate of the same grade. This mixture when packed dry into a crucible sinters together on ignition, making a lining of lime. The blast lamp used for melting the silver was specially cleaned and polished to prevent the possibility of corroded material falling into the silver. The actual melting was accomplished by directing the blast flame onto the silver in the crucible. This prevented the occlusion of oxygen by the molten metal. As a further precaution the silver was allowed to solidify in a reducing (yellow) flame. The resulting buttons were of fine appearance. They were scrubbed with ground pumice, washed and rinsed with distilled water, and kept under distilled water till used (*4*).

Miscellaneous Analytical Reagents. In the analytical procedures the best analyzed brands of reagents were used. The distilled water was the ordinary kind of the laboratory. All reagents and the water used were tested for chlorides.

Hydrochloric Acid. The hydrochloric acid solution was carefully prepared, because the results of its standardization with analytical silver and the comparison of these results with those obtained with atomic weight silver was the major work of the investigation. The best reagent acid was diluted to a density of about 1.10, and 600-ml. portions were distilled from a Richard's flask (*3*). A Jena glass tube equipped with a water jacket served as a condenser. The first and last portions of the distillate were discarded. A quantity of the acid thus prepared was diluted with conductivity water to about 0.3 N and preserved in a ceresin-lined bottle equipped with a trap so that in-going air passed through soda lime and bubbled through a portion of acid the same as that in the bottle.

Apparatus

A long-arm Troemner balance and carefully calibrated weights were used. Weighings were made with the same degree of accuracy in the analytical as in the precision procedures in order to keep the comparison of the results with atomic weight and analytical silver on an equal basis.

A Bausch and Lomb nephelometer was used in the precision measurements.

Normality of Hydrochloric Acid by Precision Method

A button of silver was dissolved in warm dilute nitric acid (water bath) in a glass-stoppered flask equipped with a bead tower for retaining any spray that might otherwise escape. The solution of silver nitrate was then diluted in the flask with two or three volumes of distilled water and boiled quietly to remove oxides of nitrogen, after which it was carefully transferred to a 500-ml. volumetric flask, diluted to the mark, and mixed.

An amount of hydrochloric acid equivalent to the silver solution (by preliminary titration) was next weighed into a 500-ml. flask, diluted to the mark, and mixed. This acid solution was then transferred to a 1500-ml. Pyrex glass flask, exactly 100 ml. of water being used in the transfer.

The silver solution was added to the hydrochloric acid solution in the Pyrex glass flask in a room lighted only by red light. Sufficient shaking was employed to make a uniform mixture. Again exactly 100 ml. of water were used in rinsing the flask. This use of the volumetric flasks and measurement of the rinse water was for the purpose of knowing with close approximation the final volume of the mixture. It was 1200 ml.

The flask was finally covered with a black cloth and allowed to stand overnight. On the following day the mixture was stirred rapidly for 15 minutes with a motor stirrer and then allowed to settle. In nearly all cases 15 minutes' settling was sufficient to give a supernatant liquid that showed no Tyndall effect. This

solution was then adjusted to equivalence of silver and chloride ions as follows:

Two 10-ml. portions of the supernatant liquid were placed in test tubes; to one, 1 ml. of 0.01 N silver nitrate solution was added and to the other, 1 ml. of 0.01 N hydrochloric acid. In nearly all cases this preliminary test showed whether silver or chloride ion was in excess. For example, to determine approximately the extent of an excess of chloride ion, several 10-ml. portions of the supernatant liquid were placed in test tubes and to the first tube 1 drop of 0.001 N silver solution was added, to the second tube 2 drops, etc. (If this method is employed for obtaining the preliminary strength of the acid, it is better to use 0.01 N silver solution in the first tests.) Usually three tubes

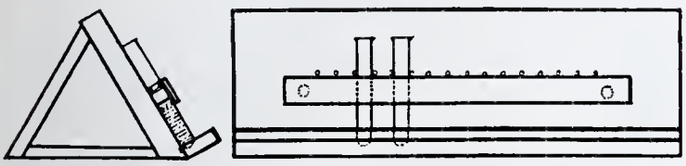

Figure 1. Test-Tube Rack Nephelometer

were sufficient. To each of these tubes an excess of chloride ion (1 ml. of 0.01 N hydrochloric acid) was added, and the opalescence produced in each case was compared with that produced by adding 1 ml. of 0.01 N silver solution to a fresh 10-ml. portion of the supernatant solution, designated as tube S. If the tube containing 2 drops of the 0.001 N silver nitrate solution matched tube S in opalescence, it is evident that the excess of chloride ions in a 10-ml. portion of the supernatant liquid was approximately equivalent to 2 drops of 0.001 N silver solution. The above procedure gives only a close approximation to the amount of silver (or hydrochloric acid) to add to the supernatant liquid to produce exact equivalence when portions are compared nephelometrically. Its advantage lies in the fact that it greatly reduces the number of trial and error tests that must be made to obtain the final equivalence.

The end point (equivalent concentrations of silver and chloride ions in the supernatant liquid) was finally produced by adding dilute silver (or chloride solution), as determined by the preliminary experiments, stirring the solution, letting settle, and then testing in the nephelometer. A small amount of silver, or chloride, solution was then added as determined by the nephelometric test and the process of stirring, etc., repeated.

The adjustment to equal opalescence was not considered final till at least three trials showed equivalent concentrations of silver and chloride ions in the supernatant liquid. In these nephelometric tests the method of Lamb, Carleton, and Meldrum (*2*) was used. This consists in heating the tubes in a water bath for 35 minutes at 45° C. Appropriate calculations were then made in order to arrive at the normality of the acid solution, the assumption being that the silver used was pure.

Weight normality (hydrogen equivalents in 1000 grams of solution) was calculated instead of volume normality. Six determinations of the normality of the acid were made in the above manner, the data of which are presented in Table I.

Table I. Normality of Acid by Comparison with Atomic Weight Silver in a Precision Nephelometer

No.	Weight of Silver	Weight of HCl Solution	Weight of HCl Solution / Weight of Silver	Weight Normality of HCl Solution
	Grams	*Grams*		
1	2.07253	65.4695	31.5891	0.29344
2	2.06605	65.2590	31.5864	0.29347
3	2.35000	74.2370	31.5901	0.29343
4	2.18111	68.9051	31.5919	0.29341
5	2.44981	77.3830	31.5874	0.29346
6	2.36681	74.7600	31.5866	0.29346
			Av. 31.5886	0.29345

An inspection of Table I shows that the maximum deviation from the average is only 0.00004 N or 0.013 per cent. The average value, 0.29345 N, was therefore accepted as the strength of the acid and used as the basis of comparison for determining the value of the analytical procedures given below.

Normality of Hydrochloric Acid by Analytical Procedures

Comparison with Atomic Weight Silver by a Simple Nephelometer. This series of experiments was made to see what effect the simplest possible nephelometric procedure would have. The conditions of the precision method were therefore observed in all particulars excepting that the final adjustment to equivalence was made in the test-tube rack nephelometer shown in Figure 1.

The essential features of this arrangement are two. The lower ends of the test tubes rest in holes in the base of the rack and the upper part of the column of liquid in the tubes is covered by a strip of wood. The rack is painted a dull black.

The procedure in using it was as follows: Two 10-ml. portions of the supernatant liquid to be tested were placed in test tubes in the rack and to one of them 1 ml. of 0.01 N silver solution was added and to the other 1 ml. of 0.01 N hydrochloric acid. If on looking down into the tubes they appeared equally bright, equivalence was assumed.

Six determinations (Table II) of the normality of the acid were made with this test-tube rack nephelometer. In all other respects the experiments were like those of Table I.

Table II. Normality of Acid by Comparison with Atomic Weight Silver in a Test-Tube Rack Nephelometer

No.	Weight of HCl Solution / Weight of Silver	Weight Normality of Acid
1	31.5891	0.29344
2	31.5853	0.29348
3	31.5901	0.29343
4	31.5919	0.29341
5	31.5887	0.29344
6	31.5828	0.29350
Av	31.5880	0.29345

Exactly the same normality was obtained as when the nephelometric comparisons were made in the more elaborate instrument. This agreement is, however, accidental, as inspection shows that the results are not as consistent among themselves. The maximum deviation from the average is 0.00005 N or 0.017 per cent. This is nevertheless very good analytical work, and shows that the test-tube rack nephelometer is a satisfactory analytical instrument.

Comparison with Analytical Silver by Precision Method. The object here was in effect to determine the purity of the analytical silver or, better stated, to compare it with the atomic weight silver. The precision method as described above was used throughout. Results are given in Table III.

Table III. Normality of Acid by Comparison with Analytical Silver in a Precision Nephelometer

No.	Silver	Weight of HCl Solution / Weight of Silver	Weight Normality of HCl Solution
1	A	31.5896	0.29344
2	A	31.5855	0.29347
3	A	31.5870	0.29346
Av.	A	31.5874	0.29346
1	B	31.5877	0.29345
2	B	31.5860	0.29347
3	B	31.5863	0.29347
Av.	B	31.5867	0.29346

The results with the analytical silver differed from those obtained with atomic weight silver by only 0.00001 N, and their agreement among themselves was even better. Nothing more is claimed, however, than that they are excellent from an analytical point of view and show that the analytical silver is a satisfactory standard.

Comparison with Analytical Silver by an All-Analytical Procedure. Since the results in Tables II and III, obtained with the simple test-tube rack nephelometer and

the analytical silver, compared favorably with those in Table I by the more laborious methods of precision measurement, the next logical step was the development of an analytical procedure that can be carried out in any laboratory. This involved the design of a simpler apparatus for dissolving the silver (Figure 2), which consists of a 100-ml. tube closed with a paraffined cork carrying a short tube (a Gooch crucible holder was used) partly filled with glass beads to prevent the escape of spray carried up by the gas generated during the solution of the silver. The upper part of the large tube was equipped with a water jacket to protect the paraffin against melting.

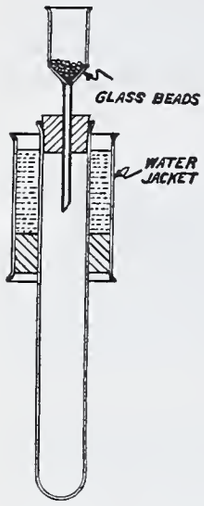

Figure 2. Apparatus for Dissolving Silver

In all strictness a special series of measurements should have been made with atomic weight silver for testing the effect of this apparatus. It was not done, however, because it seemed unlikely that the good results shown in Table IV were due to compensating errors.

The results in Table IV were obtained with the use of analytical silver dissolved in the simple apparatus (Figure 2) and by nephelometric comparisons made with the test-tube rack nephelometer.

Table IV. Normality of Acid by an All-Analytical Procedure

No.	Silver	Time	Weight of HCl Solution / Weight of Silver	Weight Normality of HCl Solution
		Hours		
1	A	4	31.5879	0.29345
2	B	17	31.5901	0.29343
3	B	3	31.5897	0.29343
4	B	5	31.5903	0.29343
5	B	18	31.5869	0.29346
6	B	5	31.5928	0.29341
7	B	7	31.5933	0.29340
8	B	4	31.5892	0.29344
		Av.	31.5900	0.29343

The average of the eight results in Table IV differed from the average of the six results by the precision method (Table I) by only 0.00002 N and the agreement among themselves is as good as that by the precision method, the maximum deviation from the average being only 0.00003 N or 0.01 per cent. This close agreement with the precision method is, of course, accidental.

The details followed in obtaining the results in Table IV were those of the suggested analytical method below. Experiments 2 and 5 show that allowing the solution to stand overnight after mixing the silver and acid solutions has no ill effect. There was considerable variation in the time necessary for arriving at equal opalescence in the final adjustment of the solutions. It should perhaps be stated that these results were all carried out one at a time.

Suggested Analytical Procedure

It is assumed that a supply of silver is at hand and that the test-tube rack nephelometer and apparatus for dissolving the silver have been made. The approximate strength of the hydrochloric acid to be standardized (distilled to insure the absence of metallic chlorides) should be known either by titration with a convenient alkaline solution or the acid can be made by diluting concentrated acid on the basis of its density and composition. Dilute solutions of silver nitrate and hydrochloric acid should also be prepared for the final adjustment to equal opalescence.

Dilute Silver Nitrate. A convenient strength is 0.0010 gram of silver per ml. It should be made by dissolving an amount of the silver to make about 250 ml. of solution.

Dilute Hydrochloric Acid. The most convenient solution is one made by weighing 50.0 ml. (call the weight P) of the acid to be standardized, transferring it to a 500-ml. flask, diluting to the mark, and mixing. One milliliter of this dilute solution will contain $0.002 \times P$ grams of the original acid solution.

Ratio of Hydrochloric Acid to Silver. A convenient technic is to use in each experiment sufficient silver to react with from 60 to 70 grams of the acid solution to be standardized. This silver is accurately weighed and dissolved in the apparatus shown in Figure 2. Oxides of nitrogen are boiled out, a little distilled water is poured through the beads to wash back any droplets that may have been carried up, and finally the solution is transferred to a 500-ml. flask in which it is diluted to the mark and mixed.

The calculated amount of the acid solution to react with the silver is then weighed from a weight buret into a 500-ml. flask where it is also diluted to the mark and mixed. This acid solution is then transferred to a 1500-ml. flask with exactly 100 ml. of water.

The 500 ml. of silver nitrate solution are next poured slowly into the acid (red light in dark room) in the large flask with rotation of the liquid to insure mixing, after which the flask is rinsed with 100 ml. of water used in several portions and the rinsings are added to the large flask, which will now contain 1200 ml. The mixture should then be motor-stirred for 30 to 40 minutes or until the supernatant liquid becomes clear after 15 to 20 minutes' settling.

The next step is the final adjustment to exact equivalence of silver and chloride ions in the supernatant liquid, which is done as in the precision method for obtaining the normality of the acid—that is, first determining the ion in excess, and then by treating three or four 10-ml. portions of the clear liquid in the test-tube rack nephelometer with 1, 2, 3, etc., drops of dilute silver or acid solution (as determined by the first test), finding the amount of silver or acid solution to add to the large flask to produce a nearer approach to exact equivalence. For the above drop testing, 10-ml. portions of the dilute solutions should be diluted to 100 ml.

The final adjustment to exact equivalence must always be made by trial-and-error additions of small amounts of dilute silver and acid solutions with intermediate motor-stirring for 5 or 10 minutes and testing in the nephelometer. The large flask should be kept covered with a black cloth or other suitable means for excluding light, so that an ordinary electric light bulb may be turned on for making the observations in the nephelometer.

Calculation

The last step is the calculation of the amounts of silver and acid used. This is done on the basis of the original weights of silver and acid, on the volume of supernatant liquid taken out for testing, and the amounts of silver and acid added for producing equivalence. The simplest way of showing how this is done is to present a typical calculation.

Weight of silver = 2.36636 grams in 600 ml. of solution
Weight of acid = 74.7501 grams in 600 ml. of solution
Total solution = 1200 ml.

1. Two 10-ml. portions of supernatant solution were removed for determining which ion was in excess. Test showed chloride in excess.
2. Four 10-ml. portions were removed for determining approximate volume of dilute silver nitrate solution to add to react with excess of chloride left in large flask. Amount found 1.5 ml. This was added to the 1140-ml. solution in flask. Calculated amount for original volume of 1200 ml., 1.58 ml.
3. Six 10-ml. portions were removed for three nephelometric tests for equivalence after addition of the 1.5 ml. of silver solution. Test showed slight excess of silver ions, and 0.5 ml. of the dilute acid was added. Calculated amount for 1140 ml., 0.53 ml.
4. Six 10-ml. portions were removed for nephelometric tests. Slight excess of chloride found, and 0.2 ml. of dilute silver solution added to the 1020 ml. in flask. Calculated amount for 1080 ml., 0.21 ml. Tests showed equivalence after this addition of silver.

The total weights of silver and hydrochloric acid solution are found by simple addition as follows:

	Grams
Original weight of silver	2.36636
1.58 ml. of dilute silver solution	0.00158
0.21 ml. of dilute silver solution	0.00021
Total	2.36815
Original weight of acid	74.7501
0.53 ml. of dilute acid = 0.053 gram of original acid	0.0530
	74.8031

The weight normality is then

$$\frac{1000 \times 2.36815}{74.8031 \times 107.88} = 0.29346\ N$$

The above specimen calculation presupposed three trial-and-error additions to bring about equivalence. In none of the actual experiments, however, was this necessary. The preliminary test described above was so effective that two additions always gave the end point.

Conclusion

Readers are likely to assume that this silver method for standardizing an acid is too cumbersome to employ. Trial will show, however, that this is not the case. The procedure appears cumbersome because it is unfamiliar, but it is, for example, no more difficult or time-consuming than the constant-boiling acid method (*1*) so often employed. Also, it is not offered as a rapid method of standardizing hydrochloric acid but rather as a reliable one.

Nothing has been said about applying vacuum corrections to the weighings. Such corrections are not necessary, since the paper deals with a comparison of two procedures, the atomic weight or precision method of standardizing and the analytical method. Owing to the small difference in density between silver and the brass of the weights, a vacuum correction applied to the weight of silver would affect the normality of the acid somewhat less than one unit in the fifth decimal place. The vacuum correction in weighing the hydrochloric acid solution would be large, but it can be avoided by the simple expedient of defining a weight normal solution as one that contains a hydrogen equivalent in 1000 grams of solution as weighed with brass weights in air.

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Estimation of Aldehydes by the Bisulfite Method

An Improved Procedure

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The bisulfite method of Ripper (*27*) was initially tested only with formaldehyde, acetaldehyde, benzaldehyde, and vanillin. A study by Feinberg (*7*) included also salicylaldehyde, *p*-hydroxybenzaldehyde, and anisaldehyde, results for these being only semi-quantitative. Jolles determined furfural and pentoses (*13*) and acetone (*12, 29*); Meyer (*25, 26*) recommends the method for several aldehydes in addition to those mentioned, but without evidence that its applicability has been tested. The bisulfite method has been used for estimation of lactic acid via acetaldehyde (*2, 3, 9, 10*), and of some unsaturated aldehydes (*11, 15, 26*). Reports as to the accuracy of the method are conflicting, in some cases because of failure to appreciate the nature of the reactions involved and the conditions essential to accuracy.

The reaction between carbonyl compounds and bisulfite is reversible:

$$\underset{|}{\mathrm{R.CO}} + {}^{-}\mathrm{HSO_3} \rightleftharpoons \underset{|}{\mathrm{R.C(OH)SO_3}}^{-}$$

The distribution at equilibrium varies with the identity of the carbonyl compound, the pH, temperature and concentration of the solution, and the excess of bisulfite. The results of analysis depend further upon the specific rates of the addition and dissociation reactions, these also being affected by the conditions mentioned. Kerp and collaborators (*14*) made equilibrium studies of the bisulfite compounds of formaldehyde (*6*), acetaldehyde, benzaldehyde, furfural, acetone, and glucose, and Stewart and Donnally (*31*) reported a more elaborate study of benzaldehyde-bisulfite. Using Kerp's data, Kolthoff (*19*) calculated the inherent error in analysis due to dissociation.

A consideration of available evidence permits the following conclusions:

1. The accuracy of analysis is determined primarily by the value of the equilibrium constant for the dissociation. When this is of the order of 10^{-4} or less, accurate analysis is feasible (formaldehyde, acetaldehyde, benzaldehyde, furfural). When K equals 10^{-3} (acetone), analysis is possible if bisulfite is used in large excess. When K is greater than 10^{-3} (glucose), the results are too low.
2. The accuracy of the method is increased, especially when K is unfavorably high, by excess of bisulfite and by increase in the concentrations of both reactants. When K equals 10^{-7} (formaldehyde) or 10^{-6} (acetaldehyde), even dilute solutions can be analyzed using only a moderate excess of bisulfite.
3. The accuracy of analysis is affected by temperature, but here two conflicting effects are to be noted. The error due to dissociation can be decreased by working at low temperature, as the value of K decreases with decreasing temperature (*14, 31*), but the rate of the addition reaction is thereby decreased, and the time necessary for attainment of equilibrium may exceed the 15 to 60 minutes usually specified. The analysis of some aldehydes requires a low temperature at the time of titration; in such cases the reaction liquid may be allowed to stand a suitable interval at room temperature and then chilled for a time before and during titration.
4. The rates of addition and dissociation are affected by the hydrogen-ion concentration, the former decreasing with increasing acidity, while the latter and the dissociation constant are at a minimum somewhat in the acid region (at about pH = 1.8 for

Table I. Analysis of Aldehydes by Modified Ripper-Feinberg and Excess-Iodine Procedures

Compound[a]	Sample	Concn. of $NaHSO_3$	Time	Temperature	Indicated Purity: Ripper-Feinberg method	Indicated Purity: Excess iodine method
	Gram	*M*	*Min.*	° *C.*	%	%
Formaldehyde						
Solution 1						
Romijn: 35.92%	0.2144	0.3	60	27	35.36	35.80
H_2O_2–NaOH: 35.95%					35.13	36.02
					35.23	35.44
					35.16	35.60
					Av. 35.22	Av. 35.72
Solution 2						
H_2O_2–NaOH: 36.29%	0.2159	0.3	30–60	23	35.43	36.54
					35.75	36.57
					35.60	36.39
					Av. 35.59	36.49
						Av. 36.50
Acetaldehyde[b]						
B. p. 24.8–25°	0.13–0.25	0.3–0.4	60	21–24	93.10[c]	97.24[d]
B. p. 22.5–25°	0.12–0.16	0.4	35	20–23	94.00[e]	98.62[e]
B. p. 21.5–21.9°	0.1681	0.4	45	22	...	98.36
	0.1433	0.4	30	23	...	98.90
	0.1298	0.4	30	24	98.00[f]	99.42
						Av. 98.89[f]
Propionaldehyde						
B. p. 48.4–48.6°	0.15–0.22	0.4	30–240	21–24	90.02[e,g]	95.53[d,g]
B. p. 48.4–48.5°	0.1673	0.4	45	26	90.20	98.38
Used promptly	0.1421	0.4	45	28	...	98.75
	0.1401	0.4	45	28	...	97.88
						Av. 98.57
n-Butyraldehyde[h]	0.1346	0.4	60	26	...	99.31
B. p. 75.4°	0.1532	0.4	60	21	...	97.90
	0.1376	0.4	60	21	...	98.26
	0.1387	0.4	60	25	93.38	98.65
	0.1587	0.4	45	25	...	98.40
						Av. 98.50
Isobutyraldehyde[h]	0.1290	0.4	60	21	...	95.66
B. p. 64.2–64.6°	0.1350	0.4	60	21	...	95.82
	0.1235	0.4	45	21	92.97	95.48
	0.1888	0.4	60	22	88.83	96.19
	0.1729	0.4	15	22	...	95.65
	0.1878	0.4	60	In ice	88.74	95.93
					Av. 90.18	Av. 95.79
n-Valeraldehyde[h]	0.1906	0.4	30	24	(88.18)	95.90
B. p. 102.4°	0.1517	0.4	45	26	94.87	95.87
	0.2055	0.4	60	24	...	96.13
	0.1626	0.4	45	In ice	97.32	97.10
					Av. 96.10	Av. 96.25
Isovaleraldehyde[h]	0.1484	0.4	45	25	92.17	97.08
B. p. 92.5°	0.1429	0.4	45	22	...	98.23
	0.1407	0.4	45	23	...	97.30
	0.1416	0.4	60	25	91.58	98.00
	0.1397	0.4	45	In ice	...	97.54
	0.1392	0.4	60	In ice	93.48	...
					Av. 92.41	Av. 97.63
n-Heptaldehyde[i]	0.1886	0.4	45	25	...	96.59
B. p. 151.4°	0.1452	0.4	45	24	91.76	97.28
Redistilled: B. p. 152.4°	0.1642	0.4	45	28	...	96.23
	0.1380	0.4	45	25	...	96.81
	0.1359	0.4	45	30[j]	89.27	97.18
	0.1399	0.4	60	32[j]	...	98.99
					Av. 90.52	Av. 97.18[k]

benzaldehyde bisulfite), and increase as the acidity diminishes (*14, 31, 32*). Practical application of these relationships was made by Tomoda (*32*) in the estimation of acetaldehyde, the excess bisulfite being titrated as usual, the pH adjusted to about 8 (sodium bicarbonate) to accelerate the dissociation of the bisulfite compound, and the bound bisulfite then titrated as a direct measure of the aldehyde. A similar procedure was described recently by Lea (*23*) for heptaldehyde. Donnally (*5*) applied a more rigid control to the analysis of formaldehyde and benzaldehyde, making three pH adjustments: one (sodium bicarbonate) for the addition, a second at about pH 2 (acetic or phosphoric acid) for titration of excess bisulfite, and a third (sodium carbonate) for titration of bound bisulfite. Such procedures are theoretically superior to the method of Ripper, afford a direct instead of an indirect analysis, and eliminate the blank analysis. The accuracy, however, is not necessarily increased, for the direct titration starts at the end point of the excess-bisulfite titration, and the imperfections in this end point will affect equally the results by both methods. Donnally obtained for formaldehyde nearly identical results by both titrations, but results for benzaldehyde were high as calculated from the titration of excess bisulfite. This is attributed to oxidation of bisulfite by air, but it is not clear why such incidental oxidation did not similarly affect the results for formaldehyde.

5. An inherent source of inaccuracy in the Ripper method is the manner of titration—the addition of iodine to bisulfite—when, as is well known, correct results are obtained only by the reverse procedure (*17, 33*). The irregularity has been assigned variously to reduction by the hydriodic acid of reaction, to loss of sulfur dioxide by volatilization, and to air oxidation of sulfite, the last being probably the chief source (*8, 16, 20, 24*). As aldehyde bisulfites are not *per se* reactive with iodine, but reduce it only at the rates at which they dissociate (*14, 21, 31, 32*), the reversal of the Ripper titration is feasible if the specific dissociation rate in any case is not too high. This modification—addition of an aliquot of the reaction liquid to a measured excess of iodine and prompt back-titration with thiosulfate—was used by one of the writers (W.) in 1925 in the early trials of the excess-iodine method described below, and was independently adopted as preferable by Kolthoff (*18*) for analysis of formaldehyde, acetaldehyde, benzaldehyde, and furfural.

This paper presents results obtained by the excess-iodine method just mentioned, in comparison with results given by a somewhat modified Ripper-Feinberg procedure, both applied to the following compounds: formaldehyde, acetaldehyde, propionaldehyde, *n*- and isobutyraldehydes, *n*- and isovaleraldehydes, *n*-heptaldehyde, acetal, benzaldehyde, salicylaldehyde, vanillin, piperonal, paraldehyde, crotonaldehyde, and cinnamaldehyde, the last three not being analyzable by the procedures used. The results show a marked superiority for the excess-iodine procedure. Under the conditions employed, the acidity of the unbuffered bisulfite was somewhat too high for the most rapid attainment of equilibrium, and especially toward the end of the titration, probably exceeded the optimum for greatest stability of the bisulfite compound. The unfavorable effect of the first condition was counterbalanced by use of a rather large excess of bisulfite of greater concentration (0.3 to 0.4 *M*) than was specified by Ripper or

TABLE I (*Continued*)

Compound[a]	Sample	Concn. of $NaHSO_3$	Time	Temperature	Indicated Purity: Ripper-Feinberg method	Indicated Purity: Excess iodine method
	Gram	*M*	*Min.*	*° C.*	%	%
Paraldehyde	0.1669	0.3	90	24	0	...
B. p. 123.6–124.4°			+21 hrs.		0	...
	+ 0.25 g. $PhSO_3H$		+75 min.		1	...
	0.2074 + 1 g. $PhSO_3H$	0.3	45 hrs.	Room	57.30	...
Crotonaldehyde	0.1592	0.4	30	22	...	178.1[l]
B. p. 102.3°	0.1842	0.4	45	22	192.7[l]	195.7[l]
	0.1568	0.4	45	24	123.2[l]	117.6[l]
	0.1595	0.4	45	25	...	96.6[l]
	0.1661	0.4	60	23	...	105.1[l]
Acetal	0.4853	0.3	60	Room	97.02	97.21
B. p. 102.4–102.7°	0.4826	0.3	60	Room	94.58	98.06
	0.4710	0.3	120	25	97.56	...
	0.4716	0.3	120	26	...	97.33
	0.4695	0.3	120	27	95.75	...
	0.4655	0.3	120	26	...	96.99
	0.4470	0.3	150	25	97.22	...
	0.4670	0.3	150	24	...	97.78
	0.4310	0.3	16 hrs.	Room	97.44	97.30
	0.6234	0.3	180	In ice	97.02	96.52
Redistilled:	0.5053	0.3	135	Room	97.23	...
B. p. 102.7–102.8°	0.4845	0.3	135	24	...	96.54
					Av. 96.73	Av. 97.22
Benzaldehyde[h]	0.2510	0.4	45	27	...	95.65
B. p. 178.5°	0.2485	0.4	45	27	(85.61)	96.35
Redistilled in N_2:	0.3936	0.4	45	28	...	96.52
B. p. 178.4°	0.2459	0.4	45	29[j]	97.45	97.69
Salicylaldehyde[h]	0.2665	0.4	45	26[j]	94.44	96.31
B. p. 196–196.3°	0.2736	0.4	45	27[j]	...	96.21
	0.2648	0.4	45	27[j]	...	95.82
						Av. 96.11
Cinnamaldehyde[h]						
B. p. 250.7–251.3°	0.2907	0.4	45	24[j]	...	175.2[l]
Vanillin[h]	0.2414	0.4	45	27[j]	...	97.89
M. p. 81.5°	0.2419	0.4	45	26[j]	96.46	96.99
	0.2464	0.4	45	24[j]	...	96.96
						Av. 97.28
Piperonal[h]	0.2278	0.4	45	25[j]	98.80	100.75
M. p. 36.6–37.0°	0.2286	0.4	45	28[j]	...	100.40
						Av. 100.58

[a] Boiling and melting points are corrected values.
[b] Boiling points for acetaldehyde affected by positive error due to superheating through column wall.
[c] Average of 7 determinations.
[d] Average of 6 determinations.
[e] Average of 4 determinations.
[f] Other workers (*10, 12, 24, 27, 28, 34, cf. 22, 30*) have reported higher values for acetaldehyde.
[g] Specimen deteriorated.
[h] 5 cc. of alcohol used.
[i] 10 cc. of alcohol used.
[j] Chilled in ice during titration.
[k] Using the direct titration (bound bisulfite) method, Lea (*23*) obtained for heptaldehyde 19 results which ranged from 93.3 to 97.0 per cent and averaged 95.6 per cent.
[l] Note irregular effect of double bond.

Feinberg. That of the second condition was decreased, in the analysis of aldehydes whose bisulfite compounds gave evidence of too rapid dissociation at room temperature, by chilling in ice (after standing at room temperature) for a short time before and during contact with iodine. (Analysis by Ripper's method at low temperature has been recommended by several chemists, *4, 30, 34*.) This precaution was advantageous in the estimation of aromatic and higher aliphatic aldehydes.

Rationalization of the bisulfite procedure must await extension of methods such as those used by Kerp et al., and by Stewart and Donnally, to other compounds, so as to permit selection of optimum conditions for addition and titration. This work is projected for the near future.

EXPERIMENTAL

REAGENTS. In most of the trials the sodium bisulfite solutions were 0.3 or 0.4 *M*. They were not stabilized (*20, 16, 24*), the effective concentration being determined for each series of analyses by means of a parallel blank. Sodium thiosulfate (0.1 *N*) was standardized weekly or oftener against potassium iodate. Iodine (0.1 *N*) was standardized frequently against the thiosulfate. Though prepared as directed by Ripper (*27*) and later by Chapin (*1*), the solutions lost strength rapidly.

ALDEHYDES. Commercial specimens of U. S. P. strength formaldehyde were used, assayed by the iodometric method of Romijn and the alkaline hydrogen peroxide method of Blank and Finkenbeiner.

Liquid aldehydes were Eastman Kodak Company products. They were shaken with sodium carbonate solution, dried with calcium chloride, and specimens of good boiling point obtained by means of an 8-ball Snyder column. If necessary, specimens were redistilled, using a semi-micro column, until maximum results were obtained by analysis. Specimens which suffered rapid air-oxidation or polymerization were redistilled before each analysis and used promptly. Benzaldehyde was finally distilled under nitrogen, and samples were collected directly in the measured bisulfite solution. The deterioration of most of these aldehydes was rapid, and in general it was found that analytical purity could be assumed only for specimens freshly purified. The deterioration of several aldehydes was plainly due to oxidation. Some deteriorated samples left droplets insoluble or slowly soluble in bisulfite solution, suggesting the presence of polymers; the trials with paraldehyde indicated that aldehyde polymers cannot be estimated by the bisulfite method.

Vanillin and piperonal were Kahlbaum specimens, recrystallized from 10 and 50 per cent alcohol, respectively.

ANALYTICAL PROCEDURES. Each analysis required two 50-cc. volumetric flasks, into each of which 25 cc. of bisulfite solution were pipetted. Into one flask was introduced the sample (0.002 to 0.004 mole) as described below. The liquids were diluted to the mark, mixed, and the stoppered flasks allowed to stand for the selected period (usually 30 to 60 minutes). An aliquot of each (usually 10 cc.) was withdrawn with a pipet calibrated against the flasks, and the titratable bisulfite determined as described below. In certain cases indicated in Table I the liquid was chilled in ice during the last 10 minutes of the standing period and throughout the determination of bisulfite.

About 2 cc. of formalin were introduced into a weighed 100-cc. volumetric flask containing about 25 cc. of water, the increase in weight was determined and the solution diluted to the mark, and 10-cc. aliquots were used for analysis.

Freshly distilled acetaldehyde was transferred to a weighed glass ampoule, which was sealed off and reweighed. The ampoule was broken under bisulfite solution in the reaction flask, the solution diluted to the mark, and a volume of water equal to that displaced by the ampoule added from a Mohr pipet.

For water-soluble aldehydes the stoppered 50-cc. flask containing 25 cc. of bisulfite solution was weighed, the sample dropped

into the liquid, and the flask reweighed. For aldehydes insoluble or slightly soluble in water, 5 cc. (in some cases 10 cc.) of aldehyde-free alcohol were stratified upon the bisulfite solution before introducing the sample. Solid aldehydes were introduced through a wide-stem funnel. When alcohol was used in an analysis an equal volume was added to the blank.

To determine excess bisulfite by the modified Ripper-Feinberg method, 10 cc. of solution were withdrawn, and the pipet was thrust nearly to the bottom of an Erlenmeyer flask and allowed to drain. Excess bisulfite was titrated at once and rather rapidly with 0.1 *N* iodine, with the addition of 5 cc. of 0.5 per cent starch indicator near the end point. With aliphatic aldehydes the end points were generally satisfactory. With aromatic aldehydes the end color was transitory, persisting only a few seconds; unless such titrations were run rapidly the approximately correct end point was inevitably overrun. To determine the effective strength of the bisulfite solution, an aliquot of the blank was similarly titrated.

To determine free bisulfite by the excess-iodine method, 50 cc. of 0.1 *N* iodine were pipetted into an Erlenmeyer flask, and a 10-cc. aliquot of the analysis liquid was allowed to flow in while rotating the flask. The excess iodine was immediately titrated with 0.1 *N* sodium thiosulfate. In some cases the flask was immersed in an ice bath during the period excess iodine was present. An aliquot of the blank analysis liquid was treated similarly. The end points by this procedure were in all cases satisfactory.

Results of trials by the two methods are given in Table I.

The results in Table I show that the excess-iodine procedure is in general superior to the modified Ripper-Feinberg method. The effect of time was not pronounced, and it appears that 45 to 60 minutes, and in some cases less time, will yield maximum values for most of the compounds tested. The effect of low temperature was generally favorable though rather small for aliphatic aldehydes, but was pronounced for aromatic aldehydes, analysis of which requires chilling of the liquid before titration. Neither method can be considered precise, except for formaldehyde, and agreement of duplicates within 0.5 per cent is in general to be considered good.

Decomposition of Aldehyde Bisulfites in Contact with Iodine

In the excess-iodine procedure some dissociation of aldehyde bisulfite must occur between the moment the aliquot is added to excess iodine and that at which the end point of the thiosulfate titration is reached. In practice this is decreased by chilling the liquid. To obtain an approximate idea as to the relative rates of dissociation of various aldehyde bisulfites in contact with iodine under the conditions of analysis, self-explanatory tests were made (Table II).

Table II. Decomposition of Aldehyde Bisulfites in Contact with Iodine

Aldehyde	Immediate Titration of Excess Iodine[a]		Titration after Extended Contact with Iodine		
	Temp.	Indicated purity	Temp.	Time of contact	Indicated purity
	° C.	%	° C.	Hours	%
Formaldehyde	Room	35.5	Room	3	35.7
Acetaldehyde	24	96.5	Room	1	93.0
	24	97.1	Room	16	89.9
	23	98.9	23	1	97.0
Propionaldehyde	23	95.0	23	0.75	93.2
n-Butyraldehyde	23	79.9	23	1	77.3
Iso-butyraldehyde	24	94.5	24	1	77.8
			35–40	1	41.8
n-Valeraldehyde	25	93.9	25	1	91.3
Isovaleraldehyde	22	98.2	22	1	92.8
n-Heptaldehyde	25	96.8	25	1	93.0
Benzaldehyde	27	95.7	27	1	51.3
Salicylaldehyde	In ice	96.2	In ice	1	70.5
			27	1	1.4
Vanillin	In ice	97.0	In ice	1	73.9
			24	1	7.4
Piperonal	In ice	100.4	In ice	1	86.4
			28	1	15.1

[a] Time of contact of aldehyde bisulfite with excess iodine not over 5 minutes.

The results in Table II indicate that the bisulfite compounds of lower aliphatic aldehydes react somewhat slowly with iodine, formaldehyde bisulfite being wholly stable. The bisulfite compounds of aromatic aldehydes dissociate much more rapidly; in ice the rate is much decreased, but is still sufficiently high to show that even with prompt titration of excess iodine a sensible negative error will enter the results.

Conclusions

The Ripper-Feinberg bisulfite method yields low results with many aldehydes because of the reversible dissociation of the aldehyde bisulfites, and because of inaccuracy in the titration of excess bisulfite by iodine. To avoid the titration error a procedure is used in which an aliquot of the analysis liquid is added to a measured excess of iodine, and the excess titrated promptly with thiosulfate. With aldehydes whose bisulfite compounds dissociate too rapidly at room temperature the liquid is chilled in ice before and during contact with iodine. Both methods have been applied to a more extended list of aldehydes than has previously been tested by the bisulfite method; the excess-iodine procedure gave the higher and more consistent results and better end points.

The aldehydes tested, and averaged purity results by the excess-iodine method, are as follows: formaldehyde (100 per cent), acetaldehyde (98.9 per cent), propionaldehyde (98.6 per cent), *n*-butyraldehyde (98.5 per cent), isobutyraldehyde (95.8 per cent), *n*-valeraldehyde (96.3 per cent), isovaleraldehyde (97.6 per cent), *n*-heptaldehyde (97.2 per cent), acetal (97.2 per cent), benzaldehyde (97.1 per cent) salicylaldehyde (96.1 per cent), vanillin (97.3 per cent), piperonal (100.6 per cent). Paraldehyde, crotonaldehyde, and cinnamaldehyde could not be satisfactorily analyzed.

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Reducing Action of Mercurous Chloride

Separation, Detection, and Estimation of Arsenic, Gold, Platinum, Palladium, Selenium, Tellurium, and Iodine

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The reducing action of mercurous chloride has been adapted specifically to new methods for the detection and approximate estimation of minute quantities of gold, platinum, palladium, tellurium, selenium, arsenic, and iodides. These methods offer a number of advantages over older methods, particularly with respect to simplicity, delicacy, and interfering substances.

Under controlled conditions the methods undoubtedly have value from an analytical as well as commercial standpoint in the recovery of these rare elements. The reaction can perhaps be applied to other rare and easily reduced elements.

A NUMBER of years ago (*1*) the writer observed that mercurous chloride would precipitate metallic arsenic from solution in concentrated hydrochloric acid and serve as an extremely delicate test for that element. Recently the reducing action of mercurous chloride on other easily reduced elements such as gold, platinum, palladium, selenium, and tellurium has been investigated and new methods based on this reaction for separating, detecting, and estimating extremely minute quantities of these elements have been worked out. Although the reaction appears to be simple and affords the most effective and delicate chemical test known to the author, the literature on the subject is apparently confined to an occasional statement in textbooks that mercurous salts reduce solutions of gold to the metallic state.

A general equation for the reaction is

$$MX + HgX = M + HgX_2$$

The specific affinities or the potentials of the system which cause the reaction to proceed from right to left depend upon the elements involved and such conditions as temperature and acidity. Although the reaction takes place with any mercurous halide, the chloride is best suited for detections and estimations because it is white. Mercurous chloride is an extremely insoluble, very fine powder which not only rapidly precipitates certain elements from their solutions but also completely adsorbs the precipitated elements which are undoubtedly of colloidal fineness. Gold so precipitated may appear cream, pink, purple, or gray, while arsenic may give a buff, pink, brown, or black color depending upon conditions. These different colors may indicate allotropic modifications or possibly degrees of fineness of the reduced elements. Mercurous chloride, being very heavy, settles rapidly, and with the precipitated elements adsorbed can be readily separated for observation or recovery. Colored solutions do not interfere with the analysis and the tendency of reduced elements to form a colloidal suspension too fine to separate or be distinguished is eliminated. The fact that mercurous chloride sublimes at a comparatively low temperature offers a simple means for recovering the salt and separating the precipitated metal in pure form.

General Method of Analysis

This work has been principally concerned with the detection and approximate estimation of minute quantities of certain elements. When an approximate estimation of quantity is desired, extremely dilute solutions must be used. The estimations are based upon the shades of color produced by the precipitated element adsorbed on the mercurous chloride powder and beyond certain limits no change in color is produced by an increased amount of precipitation. These changes of color are delicate and must be compared with standard controls carried along under exactly the same conditions as the test. Hydrochloric acid is used to control the acidity of the solution under examination and should be prepared by boiling with a small quantity of mercurous chloride and standing over the mercurous chloride for about 24 hours. In general, the procedure has been to add 0.1 gram of mercurous chloride to a clean dry 100-cc. beaker, mix in 5 cc. of distilled water or hydrochloric acid to produce the desired degree of acidity, and add from 1 drop to 1 cc. of the solution under test. Small quantities of the test solutions are preferred to keep interfering substances from reaching objectionable concentrations. With occasional shaking the reaction is complete in a few minutes, after which the mercurous chloride is allowed to settle and is collected by tilting the beaker. With heat the reaction is more rapid, but care must be taken to treat the standard controls in the same manner. In strong acid solutions high temperatures may decompose the mercurous chloride, producing a gray color which interferes and must be avoided. Pretreating the acid with mercurous chloride greatly retards the development of the gray color. It is desirable to extract the test solution with mercurous chloride and use this extracted test solution as a base to prepare the standard control.

In addition to the ease and extreme delicacy of these tests, they are also remarkably free from interference. When 1 cc. or less of the test solution is diluted to 5 cc., interfering substances are limited to those having very strong oxidizing or reducing action under the conditions of the test. Starch, dextrin, blood, and casein do not interfere. Nitrates, per salts, iodides, free halides, stannous chloride, and hypophosphites must be absent, although among this group only nitrates are likely to be encountered. Cupric and ferric salts may interfere when present in sufficient quantity, apparently by oxidizing the elements precipitated or about to be precipitated on the mercurous chloride. The amount of Cu^{++} and Fe^{+++} which produces serious interference varies for each element. The approximate tolerance limits for 5 cc. of the solution being precipitated are: gold, 0.003 gram of copper and 0.006 gram of iron; platinum, 0.003 gram of copper in the cold (no interference in boiling solutions) and 0.003 gram of iron; palladium 0.003 gram of iron (copper does not interfere); selenium, 0.0006 gram of copper and 0.010 gram of iron; tellurium 0.003 gram of copper and 0.002 gram of iron; arsenic, 0.0003 gram of copper and 0.06 gram of iron. Boiling is necessary to precipitate platinum in the presence of a relatively large amount of the cupric ion, while palladium precipitates readily in a cold or warm solution. The specific effect of cupric salts is used as a means of separating platinum and palladium.

Gold. Many methods have been proposed for detecting traces of gold in solution, but have found limited application because they can be applied only to colorless solutions free from many possible interfering elements. The mercurous chloride test is far more simple and delicate, and colored solutions are no hindrance.

The ordinary methods usually precipitate gold from very dilute solutions as a colloidal suspension or slime which is very difficult to settle or remove by filtration. Mercurous chloride adsorbs the precipitated metal and provides a mixture which is extremely easy to separate by filtration or sedimentation. Because of the extreme insolubility of some forms of powdered mercurous chloride, the loss of this salt is practically limited to the more soluble mercuric chloride formed by the reduction of an equivalent amount of gold. A number of experiments have been made by the author in order to determine the practicality of recovering gold from sea water. Using synthetic sea water containing one part of ionized gold in one hundred million parts of water, recoveries have been made at an estimated cost which indicates this process to be something decidedly more than a romantic possibility. In mixtures of gold and mercurous chloride the mercurous chloride can easily be sublimed and recovered by condensation leaving pure gold. Gold precipitates completely and rapidly from a neutral or acid solution and less than 0.00005 mg. can be detected by a faint coloration with 0.1 gram of mercurous chloride. For quantitive estimations it is best to use a quantity of gold solution sufficient to give the purplish pink shades. The colors produced on this quantity of mercurous chloride are:

Gold *Mg.*	Color on Mercurous Chloride
0.20	Dark purple
0.10	Pinkish purple
0.05	Purplish pink
0.02	Strong pink
0.002	Light pink
0.0002	Very light pink
0.00005	Faint coloration

Palladium. Apparently no method suitable for the detection and approximate estimation of very small amounts of palladium in dilute solution has been described in the literature. Mercurous chloride precipitates metallic palladium from a neutral or acid solution, and in solutions comparatively free from interfering substances it is possible to detect 0.00005 mg. by the slight cream coloration on 0.1 gram of mercurous chloride. The approximate colors produced on this quantity of mercurous chloride by different amounts of palladium are:

Palladium *Mg.*	Color of Mercurous Chloride
0.2	Very dark gray
0.05	Gray
0.01	Light gray
0.002	Cream gray
0.0004	Grayish cream
0.00005	Faint cream

Platinum. The literature gives no simple or delicate method of detecting and estimating minute quantities of platinum in dilute solution. Mercurous chloride precipitates platinum from neutral or acid solutions. The smallest quantity which gives a slight coloration on 0.1 gram of mercurous chloride is about 0.0002 mg. The approximate colors for this amount of mercurous chloride are:

Platinum *Mg.*	Color on Mercurous Chloride
0.1	Dark gray
0.02	Gray
0.01	Creamish gray
0.005	Grayish cream
0.001	Cream
0.0002	Slight cream

Platinum and palladium precipitate under similar conditions and the coloring on the mercurous chloride is also similar. However, a suitable concentration of copper sulfate prevents the precipitation of platinum except after boiling, while palladium precipitates readily from a cold or warm solution. The specific effect of copper sulfate offers an effective means of separating mixtures of platinum and palladium in solution.

Selenium. Selenium is precipitated by mercurous chloride only from solutions containing 6 to 20 per cent of hydrochloric acid, and is not complete with less than 16 per cent. With an optimum of 20 per cent acid it is possible to detect 0.0002 mg. The colors produced on 0.1 gram of mercurous chloride are approximately:

Selenium *Mg.*	Color on Mercurous Chloride
0.2	Salmon red when cold, bright red when warm
0.05	Salmon pink
0.005	Strong pinkish cream
0.002	Pink cream
0.0005	Light cream
0.0002	Faint cream

Mercurous chloride precipitates tellurium under the same conditions as selenium; therefore these elements must be separated to be detected or estimated by mercurous chloride. Sodium bisulfite completely precipitates selenium from a solution containing approximately 20 per cent of hydrochloric acid, while tellurium remains in solution. The selenium can be filtered, redissolved, and estimated by the usual mercurous chloride method.

Tellurium. This element like selenium is not precipitated from solutions containing less than 6 per cent hydrochloric acid and precipitation is not complete in solutions containing less than 15 per cent acid. About 20 per cent of hydrochloric acid is used in the standard test procedure which permits the detection of about 0.0005 mg. of tellurium. The colors produced by the precipitation are approximately:

Tellurium *Mg.*	Color on Mercurous Chloride
0.2	Grayish yellow, turns grayish brown when hot
0.05	Cream yellow
0.005	Light cream yellow
0.0005	Faint cream

Arsenic. A number of methods are available for detecting or estimating minute quantities of arsenic, but are not without objectionable features. The Marsh and Gutzeit methods require special apparatus and an experienced operator to give the best results. The Reinsch test is simple and rapid but does not permit a good quantitive estimation, and a large number of elements interfere. The Bettendorf and Bougaults tests are short and positive under favorable conditions but are not satisfactory with colored solutions or in the presence of many other easily reduced elements. The recently studied Gosio test (*2*), depending upon the action of certain molds, does not appear to be as practical for general purposes as the strictly chemical methods.

Mercurous chloride precipitates arsenic from concentrated hydrochloric acid solutions. Arsenious solutions react rapidly and completely, while arsenates react slowly or incompletely. However, arsenate solutions can be easily reduced by sulfurous acid either before or after the addition of mercurous chloride. Practically all elements, such as gold, platinum, palladium, tellurium, selenium, and iodine, which would interfere with the reaction as a test for arsenic can be easily and quickly removed by making the test solution up to about 20 per cent hydrochloric acid and treating it with a substantial excess of mercurous chloride. Arsenic remains in solution, while the other elements are precipitated. In a warm solution with occasional shaking the separation is complete in a few minutes, after which the solution may be decanted or filtered. The hydrochloric acid concentration should then be increased to 30 per cent or higher, and arsenic precipitated by mercurous chloride. Working with pure solutions, less than 0.00001 mg. of arsenic will produce a visible shade of cream color on mercurous chloride. Using the proportions previously described for the standard test the colors produced are approximately as follows:

Arsenic *Mg.*	Color on Mercurous Chloride
0.1	Bright deep brown
0.01	Pinkish brown
0.001	Pink
0.0001	Cream
0.00002	Very slight cream

This method requires no special apparatus, the manipulation is extremely simple and short, colored solutions do not mask the precipitate, interfering substances are very few and easily reduced to a minimum, and its delicacy apparently exceeds all other methods by a substantial margin. Its accuracy for approximate estimations greatly exceeds the other wet precipitation methods. Although no comparison has been made, it seems likely that the Gutzeit method might prove more definite and accurate for estimating purposes.

Iodine. When mercurous chloride is added to a solution containing iodides, mercurous iodide forms on the surface of the particles of mercurous chloride, producing shades of color varying

from greenish black to light yellow depending upon the iodide concentration. In the absence of interfering elements less than 0.003 mg. of iodine produces a faint coloration on 0.1 gram of mercurous chloride. The shades of color produced provide a method for approximately estimating minute quantities of iodine in dilute solution.

Separation of Gold, Platinum, Palladium, Selenium, Tellurium, and Arsenic

The methods of separation are based entirely on reductions from solution to the elemental form. It is best to use very dilute solutions and to work with a few cubic centimeters of a solution containing no more than a few milligrams of each element. Such a solution should first be made acid to the extent of about 1 or 2 per cent with hydrochloric and divided into two parts, one part being treated for the segregation of gold, platinum, and palladium and the other for arsenic, selenium, and tellurium.

1. Separation of Gold, Platinum, and Palladium. Add crystals of oxalic acid to make about a 5 per cent solution and boil to precipitate gold. Filter on a fine paper, wash, then dissolve precipitate, some of which adheres to the beaker, with dilute chlorinated hydrochloric, boil off chlorine, and test with mercurous chloride to detect and estimate gold. The filtrate from the gold reduction contains the other elements from which platinum and palladium can be separated.

Evaporate filtrate to near dryness with a little sulfuric acid to decompose oxalic acid. Any element precipitated during the evaporation is dissolved with a little hydrochloric acid and potassium chlorate. Drive off free chlorine and excess acid, and dilute with water, keeping the hydrochloric acid concentration below 4 per cent. Add $CuSO_4 \cdot 5H_2O$ to make a 5 per cent cold solution, followed by mercurous chloride which precipitates palladium. The palladium may be estimated by the color on the mercurous chloride, or preferably the precipitate may be filtered, dissolved, and diluted for estimation by mercurous chloride. The filtrate from the removal of palladium now contains platinum.

Add a little mercurous chloride to the filtrate and boil gently for about 5 minutes to precipitate platinum. The precipitate may be filtered, dissolved, and reprecipitated for estimation.

2. Separation of Selenium, Tellurium, and Arsenic. Gold, platinum, and palladium are removed from this fresh solution by mercurous chloride, after which the filtrate is made up to a hydrochloric acid concentration of about 20 per cent. Add about 5 per cent of sodium bisulfite and allow to stand for 15 minutes, followed by gentle boiling for a few minutes to precipitate selenium. The selenium may be filtered, redissolved with chlorinated hydrochloric acid, and estimated with mercurous chloride. The filtrate from the removal of selenium contains tellurium and arsenic.

Tellurium is removed by adding mercurous chloride, warming the solution if necessary to hasten reaction. The filtrate now contains only arsenic.

In order to remove arsenic the hydrochloric acid concentration must be raised to 30 per cent or higher, after which arsenic can be precipitated by mercurous chloride in the usual manner.

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Determination of the Common and Rare Alkalies in Mineral Analysis

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Methods are described which afford a determination of each member of the alkali group and are successful in dealing with the quantities of the rare alkalies found in rocks and minerals. The procedures are relatively rapid and based chiefly on the use of chloroplatinic acid, absolute alcohol and ether, and ammonium sulfate. The percentages of all the alkalies found in a number of minerals are given.

In most rock and mineral analyses on record no mention is made of rubidium and cesium. Lithium is reported as a trace in many—but this means little quantitatively—though it has of course been determined occasionally by the Gooch method. The few reported results for rubidium and cesium are questionable. A method for all the alkalies is needed, one that will not be too complicated and that will be adapted to the particular purpose of handling the percentages of lithium, rubidium, and cesium met with in rocks and minerals.

Previous attempts to deal with all the alkalies are noted by Hillebrand and Lundell (*2*) and by Noyes and Bray (*4*). The method of extracting rubidium and cesium chlorides from potassium chloride by means of hydrochloric acid and alcohol has been used by several analysts. Strecker and Diaz, however, in referring to this step (*8*) give no details of procedure, and the extraction of rubidium was found to be incomplete by Moser and Ritschel (*3*); they, however, used relatively large quantities of the two salts in their tests. Experience shows that efforts should be directed to dealing with small quantities of lithium, rubidium, and cesium.

Attempts to devise a quantitative procedure on the scheme of Noyes and Bray gave unsatisfactory results for small quantities of rubidium and cesium, as the precipitates formed were not sufficiently insoluble. Results were correct only to a milligram or more. A complex organic compound, sodium 6-chloro-5-nitrotoluene-*m*-sulfonate, is suggested by Davies (*1*) as a precipitant of potassium and rubidium, the cesium compound being quite soluble. The writers found, however, that the rubidium compound was not sufficiently insoluble for the separation of rubidium from cesium.

More recently O'Leary and Papish (*5*) have reviewed the analytical reactions of rubidium and cesium and proposed some new methods. They precipitate rubidium and cesium with phosphomolybdic acid and obtain excellent separations from potassium, although the procedure appears to be rather time-consuming. Separation of most of the potassium, the element generally in excess, however, seems preferable to precipitation of the minor elements first.

The methods here described afford a determination of each member of the alkali group and are successful in dealing with the quantities of the rare alkalies found in rocks and minerals. They presuppose that the alkali chlorides have first been obtained free from all other compounds. Should magnesium and calcium be present they will be found mainly with lithium, and sulfate will be found with sodium. The behavior of traces of borate and fluoride has not been determined, but these may easily be removed if known to be present. Spectroscopic confirmation of the presence of mere traces of any of the alkalies should of course be obtained. At the present time the J. Lawrence Smith method seems to be preferred for extracting the alkalies from silicate rocks and minerals. It has long been used almost exclusively in the U. S. Geological Survey

and is also recommended by Washington (*9*), and if carefully followed will provide alkali chlorides of sufficient purity.

Reagents and Apparatus

The salts used for reference were of analytical purity. Some sodium chloride of exceptional purity was available. Potassium chloride was Baker's analytical reagent. Cesium chloride from Eimer and Amend was found to be pure by the spectroscope and on analysis gave an atomic weight of 132.29 for cesium. The rubidium chloride from Eimer and Amend analyzed as follows: H_2O, 0.44; LiCl, 0.18; NaCl, 0.36; KCl, 4.10; CsCl, 1.26; RbCl, 93.66; apparent atomic weight of Rb, 82.1. This salt was purified by fractional precipitation with chloroplatinic acid to free it from potassium, lithium, and sodium, the rubidium chloroplatinate was converted into chloride by removal of platinum by redistilled formic acid, and reprecipitated with hydrochloric acid gas and alcohol to remove any remaining cesium. After two such treatments the atomic weight found for the rubidium was 85.34. Most of the experiments involving rubidium were made with the salt having the analysis first given and corrections were applied for the impurities if necessary. These results were checked in essential particulars, however, with the purest rubidium chloride.

Most of the reagents for the methods described are available in every laboratory or can easily be procured. For the separation of cesium certain reagents are needed in particular concentrations:

Ammonium Sulfate Solution. Five grams of ammonium sulfate in 100 ml. of water.

Alcoholic Ammonium Sulfate. Dissolve about 1 gram of ammonium sulfate in 20 ml. of water and add slowly with stirring 100 ml. of 95 per cent alcohol. Remove by filtering the excess ammonium sulfate that precipitates and to the clear liquid add a few crystals of ammonium sulfate to keep it saturated. This solution contains about 0.54 gram in 100 ml.

Wash Solution. Prepare in the same way as the alcoholic ammonium sulfate, except that 0.16 gram of ammonium chloride is also added to the water solution of ammonium sulfate before addition of the alcohol.

Filtering was usually done with suction applied to a small bell jar containing a test tube or small graduate to receive the filtrate, and a filter containing a small plug of glass wool covered with asbestos or through a small sintered-glass filtering crucible. A milliliter-graduated pipet and a 10-ml. buret are needed. For the separation of cesium the suction filter apparatus consisted of a bottle with bottom removed and rubber stopper carrying funnel and suction outlet tube. The bottom was ground smooth to make an air-tight connection with a greased ground-glass plate. A small wad of glass wool was placed in the bottom of the funnel and asbestos soup poured in to make a small dense filter. The filter was washed thoroughly with water and dried with alcohol before use. The same filter may be used repeatedly. The funnel stem dipped through a perforated watch glass into the platinum dish or crucible which received the filtrate.

The "radiator" used for evaporating off ammonium sulfate consisted of a 100-ml. porcelain crucible in which was placed a small porcelain support to hold the crucible being ignited. Heat was applied to the bottom with a Bunsen flame.

Separation of Sodium and Potassium Groups

In the Smith method the total alkalies are generally weighed as chlorides, but the separations outlined in the present paper permit each alkali to be weighed separately, so that an initial weighing of the chlorides is merely a check. Ammonium chloride must of course be removed.

The alkali chlorides are first separated into two groups by the use of chloroplatinic acid; lithium goes with the sodium, and rubidium and cesium go with the potassium. This separation should be conducted with care to remove sodium and lithium as completely as possible from the potassium group. The potassium chloroplatinate group is then weighed. The chloroplatinates are changed back to chlorides by precipitating the platinum with hot dilute formic acid. If the potassium chloroplatinate group is collected and weighed in a small Jena glass filtering crucible (fineness 4), the hot formic acid may be run through the filter several times, leaving the platinum on the filter. A further trace of platinum generally separates on evaporating the alkali chloride solution to dryness, so that it is better to remove the chloroplatinates to a dish and make two evaporations with formic acid before filtering off the platinum. The sodium chloroplatinate solution is also evaporated twice to dryness with a little formic acid, and the salts are dissolved in water and filtered from the platinum.

Lithium

Having obtained the chlorides by removal of the platinum, the sodium solution is ready for the determination of lithium. This is now done in the U. S. Geological Survey by a slight modification of the excellent Palkin method (*6*) rather than by the Gooch method requiring the use of obnoxious amyl alcohol.

Procedure. Evaporate the solution of chlorides to dryness, preferably in a small glass-stoppered Erlenmeyer flask of about 30-ml. capacity. Dissolve in 0.4 ml. of water, warming slightly if necessary, cool, add 0.01 ml. of concentrated hydrochloric acid and 5 ml. of absolute alcohol, rotate the flask, add 15 ml. of ether, allow to stand about 15 minutes, filter through asbestos on glass wool in a small funnel with suction (or through a Jena sintered-glass filter or a weighed Gooch crucible for direct weighing of sodium chloride), wash well with a mixture of 1 part of alcohol to 4 or 5 parts of ether, finally evaporate the filtrate with a slight excess of sulfuric acid in a weighed dish, and heat to constant weight as lithium sulfate.

Palkin recommends a second treatment of the first lithium-bearing filtrate, but more sodium chloride is seldom obtained in a second treatment. With a zinnwaldite mica from Virginia 1.92 per cent of lithium oxide was found by this method as compared with 1.85 found by J. J. Fahey, of the Geological Survey, with the older Gooch amyl alcohol method.

Sodium

Sodium is weighed as chloride, after separation of the lithium chloride, or as sulfate.

Extraction of Rubidium and Cesium from Potassium

As already stated, Strecker and Diaz (*8*) give few details regarding the extraction of rubidium and cesium chloride from potassium chloride with hydrochloric acid–alcohol mixtures. A number of experiments were therefore made on this point, with the object of reducing the solubility of the potassium chloride as completely as possible. It was found that reduction of the percentage of water was advantageous—for example, dissolving the chlorides (0.1000 gram) in only 0.4 ml. of water, saturating with hydrochloric acid gas, and adding 10 ml. of anhydrous alcohol previously saturated with hydrochloric acid gas gave the following results:

Table I. Solubility of Alkali Chlorides at 25° C.

Solvent	Solubility KCl	Solubility RbCl	Solubility CsCl
	Grams	*Grams*	*Grams*
10 ml. of water	3.08	7.28	12.7
10 ml. of 1 volume of concentrated HCl and 2 volumes of alcohol	0.0031	0.021	0.31
0.4 ml. of water and 10 ml. of alcohol, both saturated with HCl	0.0006	0.0027	0.024

The separation of cesium from potassium is easier than separation of rubidium from potassium. The solubility indicated that about 2.7 mg. of rubidium chloride might be extracted from potassium chloride without carrying more than 0.6 mg. of potassium chloride, but tests show that the extraction of rubidium proceeds slowly. The quantities extracted (Table II) were all actually determined as chloroplatinates,

and the total chlorides first weighed were greater by about 0.6 mg. in each test, because of the presence of potassium chloride. This figure may be used as a correction on the weight of the extracted chlorides for each extraction. For these tests the flasks stood overnight and were then brought to 25° C., but similar results were obtained after 30 minutes.

Table II. Extraction of a Little Rubidium and Cesium from a Large Proportion of Potassium

(Using HCl gas and 10 ml. of alcohol saturated with HCl)

Expt.	Taken KCl	Taken RbCl	Taken CsCl	No. of Extractions	Found RbCl	Found CsCl
	Gram	*Gram*	*Gram*		*Gram*	*Gram*
1	0.1000	0.0010	....	1	0.0005	....
				2	0.0002	....
				3	0.0001	....
				Total	0.0008	
2	0.1000	0.0024	....	1	0.0014	....
				2	0.0007	....
				3	0.0003	....
				Total	0.0024	
3	0.1000	0.0058	....	1	0.0026	....
				2	0.0012	....
				3	0.0011	....
				4	0.0003	....
				5	0.0003	....
				6	0.0002	....
				Total	0.0057	
4	0.1000	....	0.0010	1	....	0.0010
				2	....	0.0000
				Total		0.0010
5	0.1000	....	0.0030	1	....	0.0028
				2	....	0.0001
				Total		0.0029
6	0.1000	....	0.0090	1	....	0.0088
				2	....	0.0002
				Total		0.0090

It may be safely concluded that if the first extract under the conditions specified is not greater than 0.6 mg., significant proportions of rubidium and cesium are absent, and accordingly no further time need be spent in looking for them, unless spectrographic tests are of interest.

Procedure. Evaporate the "potassium chloride" to dryness in a 30-ml. Erlenmeyer flask, preferably one with a glass stopper, at about 106° C. in an oven through which the neck of the flask emerges, or on the steam bath. Cool, add 0.4 ml. of water, warm, cool again, and saturate with hydrochloric acid gas from a small generating flask, by dropping concentrated hydrochloric acid into concentrated sulfuric acid. Then add 10 ml. of absolute alcohol, also previously saturated with hydrochloric acid gas. Filter with suction through asbestos in a small funnel or through a sintered-glass filtering crucible. Wash with a displacement wash of 2 ml. of a mixture of absolute alcohol and ether. Evaporate the filtrate to dryness, ignite very slightly, but not to redness, and weigh. If the weight is not more than 0.6 mg., rubidium and cesium are absent, except for spectrographic traces.

Cesium

If the weight of chlorides extracted from the potassium chloride is more than 0.6 mg., rubidium or cesium or both may be present. Very nearly all the cesium is found in the first extract, but if this is appreciable a second extract should be made to remove any further cesium. Considerable rubidium may still remain with the potassium. The next step is to remove rubidium (and potassium) as sulfate from the extracts containing the cesium. The method here described was worked out by the junior author (R. E. S.).

Potassium and rubidium are precipitated by ammonium sulfate in alcoholic solution. The quantity of ammonium sulfate, determined by many trials, is such that 5 to 10 mg. of rubidium sulfate are precipitated essentially free from cesium. A larger quantity of ammonium sulfate causes the precipitation of some cesium. Ammonium chloride is included in the alcoholic wash solution, together with ammonium sulfate to prevent precipitation of cesium sulfate during washing.

Procedure. To the dry alkali chlorides in a small dish or beaker add 0.1 ml. of 5 per cent ammonium sulfate and stir the solution until all alkali chlorides dissolve. To the solution add 5 ml. of the alcoholic ammonium sulfate from the buret, dropwise with stirring. After a few drops of the solution have been added the sulfates of potassium and rubidium begin to form as a bulky precipitate. It is well to add the first milliliter very slowly, about one drop a second, as a coarser precipitate is thus formed. Now allow the solution to stand a half hour with occasional stirring and then filter with mild suction through the asbestos pad. Rinse the precipitate, beaker, and filter thoroughly with three portions of the wash solution, about 0.5 ml. each. A wash bottle giving a fine jet is useful for the purpose. Catch the filtrate and washings, containing the cesium, in a small tared platinum crucible or dish, and add a small quantity of powdered ammonium sulfate to convert cesium chloride to sulfate during the ignition to follow. Evaporate the filtrate on the steam bath until the salts begin to crystallize, and then add a few drops of alcohol. This precipitates the salts in a finely divided condition, making them easier to dry and ignite. After taking to apparent dryness, dry the residue further by addition of a few more drops of absolute alcohol and again evaporate.

Cover the crucible with a watch glass and place in the radiator for the final drying of the residue and the removal of ammonium salts. A low flame is used; any salt which may spatter is reflected back into the crucible by the watch glass. When ammonium chloride is seen on the watch glass it may be removed and the heat increased. After the ammonium chloride is all removed the mass begins to melt and ammonium sulfate to volatilize. Care should be taken to avoid loss of cesium through spattering. After most of the ammonium sulfate is removed, apply the full flame of the burner to the radiator for a short time, then move the crucible about in the direct flame of a burner, keeping the entire crucible at moderate redness. Place in a desiccator, covered with a watch glass, cool, and weigh. Repeat until a constant weight is obtained.

Cesium may be confirmed with the spectroscope, using 2 or 3 drops of water to dissolve the sulfate in the crucible. Dip a tight coil of platinum wire, consisting of six to a dozen loops, into the solution and hold in the Bunsen flame to make the observation. A quantity of cesium even less than 0.1 mg. can thus be detected.

Dissolve the precipitate formed in the treatment with alcoholic ammonium sulfate in water, take to dryness in a second tared

Table III. Separation of Cesium and Rubidium

Expt.	Taken RbCl	Taken CsCl	Found Rb_2SO_4	Found RbCl	Found Cs_2SO_4	Found CsCl	Error RbCl	Error CsCl
	Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
7	....	0.0104	....	....	0.0113	0.0105	.....	+0.0001
8	....	0.0202	....	....	0.0214	0.0199	.....	−0.0003
9	....	0.0312	....	....	0.0323	0.0301	.....	−0.0011
10	0.0100	....	....	0.0095	....	....	−0.0005	.....
11	0.0047	....	....	0.0043	....	....	−0.0004	.....
12	0.0030	....	....	0.0028	....	....	−0.0002	.....
13	0.0010	....	....	0.0008	....	....	−0.0002	.....
14	0.0027	0.0301	0.0043	0.0039	0.0306	0.0285	+0.0012	−0.0016
15	0.0100	0.0320	0.0107	0.0097	0.0349	0.0325	−0.0003	+0.0005
16	0.0097	0.0228	0.0103	0.0093	0.0251	0.0234	−0.0004	+0.0006
17	0.0100	0.0024	0.0108	0.0098	0.0027	0.0025	−0.0002	+0.0001
18	0.0049	0.0306	0.0054	0.0049	0.0325	0.0303	0.0000	−0.0003
19	0.0049	0.0201	0.0051	0.0046	0.0220	0.0205	−0.0003	+0.0004
20	0.0046	0.0109	0.0048	0.0044	0.0120	0.0112	−0.0002	+0.0003
21	0.0050	0.0021	0.0052	0.0047	0.0026	0.0024	−0.0003	+0.0003
22	0.0020	0.0206	0.0025	0.0023	0.0217	0.0202	+0.0003	−0.0004
23	0.0021	0.0104	0.0022	0.0020	0.0113	0.0105	−0.0001	+0.0001
24	0.0018	0.0032	0.0019	0.0017	0.0034	0.0032	−0.0001	0.0000
25	0.0005	0.0008	0.0004	0.0004	0.0008	0.0007	−0.0001	−0.0001

crucible, ignite, and weigh to give the weight of rubidium and potassium sulfates in the first extracts.

Separation of Cesium and Rubidium

Experiments were made on a range of mixtures, containing quantities of cesium chloride up to 30 mg. and of rubidium chloride up to 10 mg., to illustrate the use of the method and the errors involved. Complete precipitation of the small quantity of potassium, left after treatment with hydrochloric acid and alcohol, was shown by an experiment with 2 mg. of potassium chloride. The crucible used to weigh the alkalies in the cesium fraction gave no change in weight, showing that potassium is quantitatively precipitated as sulfate. It was thought that sodium might also be removed completely, as its solubility as sulfate in water is less than that of potassium, but experiments showed that about 0.7 mg. of sodium sulfate remained in the filtrate, enough to affect the results and make spectroscopic identification of cesium difficult. To a still larger extent lithium remains in solution; an experiment with 0.0025 gram of lithium chloride yielded 0.0030 gram of lithium sulfate in the cesium fraction. Care must therefore be taken in the chloroplatinate procedure in order to avoid the presence of lithium and sodium with the cesium.

The method works best for mixtures containing up to 10 mg. of rubidium chloride and not more than 20 mg. of cesium chloride. With more rubidium its removal becomes somewhat incomplete, and with more cesium chloride it also begins to precipitate as sulfate. If larger percentages of these elements are present, an aliquot portion of the potassium group should be taken for analysis or preliminary fractional separations made. The results given in Table III were obtained at a room temperature of about 22° C., but during hot weather slightly different results were obtained and it was found necessary to cool the solutions.

On account of the difficulty of manipulating very small weights of material, temperature fluctuations, etc., the errors shown in Table III have a relative rather than an absolute significance. Nevertheless they offer the possibility of making some corrections. When the quantities of the two chlorides involved are small, as in experiments 23 to 25, no corrections are indicated. The removal of larger quantities of rubidium is less complete and a correction of about 0.3 mg. is shown. With 30 mg. of cesium chloride the results are dependent on the quantity of rubidium chloride that accompanies it; if little or no rubidium is present the results are low by about 1.3 mg., but when 10 mg. of rubidium chloride are also present the results are high by about 0.4 mg. This behavior is due to the removal of the sulfate ion as rubidium sulfate.

A trace of cesium was sometimes observed by means of the spectroscope in the rubidium separated in this way, but that the separations were not due to a compensation of errors is clearly shown by the results with the single salts. Even less than 0.1 mg. of cesium sulfate can be shown by the spectroscope and a spectroscopic quantity would have little significance in the separations.

Rubidium

If the cesium calculated to cesium chloride, plus 0.6 mg. of potassium chloride for each extraction with alcohol and hydrochloric acid, accounts for all the salts extracted, rubidium is absent; otherwise some rubidium is present, but that separated from the cesium may be only part of the total rubidium. If rubidium is found here the extraction of the potassium chloride with alcohol and hydrochloric acid is repeated as long as any more rubidium chloride is extracted, allowing 0.6 mg. of potassium chloride for each extract. The small quantities of rubidium ordinarily found in succeeding extracts may be freed from the little potassium present by separation as chloroplatinate in 5 ml. of 15 per cent alcohol, as shown below. The calculated weight of rubidium chloride can then be checked by the weight of rubidium chloroplatinate.

Separation of a Little Potassium from Rubidium and Cesium

As both rubidium and cesium chloroplatinates are considerably less soluble than potassium chloroplatinate at ordinary temperature (7), rubidium and cesium may be separated from 1 or 2 mg. of potassium chloride, as obtained in the extractions with alcohol and hydrochloric acid. The chlorides are evaporated nearly to dryness with a slight excess of chloroplatinic acid, the salts well stirred with 5 ml. of 15 per cent alcohol, and the less soluble chloroplatinates filtered off, washed with 95 per cent alcohol, and weighed. Tests of this procedure are shown in Table IV. The analyses in Table II also confirm the reliability of such separations.

Table IV. Separation of Rubidium and Cesium from a Little Potassium as Chloroplatinates

(Using 5 ml. of 15 per cent alcohol)

Expt.	Taken KCl	Taken RbCl	Taken CsCl	Found KCl	Found RbCl	Found CsCl
26	0.0040	....	....	0.0020[a]	....	....
27	0.0020	....	....	0.0001[a]	....	....
28	0.0016	0.0006	....	....	0.0008	....
29	0.0016	0.0010	....	....	0.0007	....
30	0.0015	0.0019	....	....	0.0021	....
31	0.0002	0.0038	....	....	0.0037	....
32	0.0015	....	0.0005	....	....	0.0005
33	0.0015	....	0.0010	....	....	0.0009
34	0.0015	....	0.0020	....	....	0.0020
35	0.0000	....	0.0040	0.0000[b]	....	0.0038

[a] K_2PtCl_6 precipitated, the rest being soluble.
[b] By spectroscope.

The total quantity of rubidium is the sum of that separated from the cesium in the first two extractions and that obtained in further extractions of the potassium chloride with alcohol and hydrochloric acid.

Potassium

Potassium is generally calculated from the weight of chloroplatinates corrected for rubidium and cesium, but if its percentage is small it is preferable to weigh it as chloride or sulfate obtained after separation of rubidium and cesium.

Results with Minerals

In Table V are given results on the alkalies for several minerals analyzed by the writers.

Table V. Alkalies in Certain Minerals

	Li_2O %	Na_2O %	K_2O %	Rb_2O %	Cs_2O %
Zinnwaldite from Amelia County, Va.	1.92	0.74	9.58	1.04	0.10
Biotite from Custer County, S. Dak.	0.65	0.45	8.50	1.46	1.14
Beryl from Custer County, S. Dak.	0.95	1.70	0.23	0.09	1.38
Vermiculite from Yellow Mt., Macon County, N. C.	0.04	0.20	2.66	None	0.02
Beryl, Buckfield, Maine	0.56	0.96	0.14	None	0.44
Beryl, Warren Depot, Maine	0.82	1.58	0.06	0.06	0.76
Beryl, near Standish, Maine	0.70	1.02	0.08	None	Trace

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Determination of Antimony in Solder

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THE determination of small amounts of antimony in solder continues to be perplexing to the analyst. When a sample of purest commercially obtainable solder, which contains possibly 0.002 to 0.004 per cent of antimony and approximately 0.01 per cent of arsenic, is submitted for analysis to commercial laboratories, results ranging from 0.05 to 0.25 per cent or occasionally as high as 1 per cent of antimony are invariably reported.

One investigation which may be considered typical and which clearly indicates the need for a sound, reliable method for the determination of antimony in solder, was made as follows:

A number of 150-gram samples of solder were poured from the same batch of pure metal (these were used in all subsequent analyses and investigations). Seven of the samples were submitted for analysis to leading analytical and engineering laboratories (designated as A, B, C, D, E, F, and G), care being taken to select well advertised firms of national and international standing in the field of metal analysis. To four additional samples sufficient antimony was added to make the antimony content exactly 0.12 per cent, the permissible limit for Class A solder alloy as defined by the American Society for Testing Materials; these were submitted to laboratories A, B, C, and D.

The results tabulated in Table I show antimonial contents of 0.05 to 0.51 per cent on solder which contains no antimony, and 0.18 to 0.27 per cent on Class A solder, thus eliminating both alloys in most cases from the preferred Class A status.

Table I. Antimony Found in Solder

Analyst	Pure Solder (Sb 0.003%)	Class A, A. S. T. M. Solder (Sb 0.12%)
	%	%
A	0.13	0.23
B	0.07	0.18
C	0.20	0.27
D	0.05	0.19
E	0.51	——
F	0.18	——
G	0.21	——

Unfortunately, the literature is of little assistance in this problem. The ordinary gravimetric methods involving precipitation of the sulfides, followed by separation of the antimony from tin, are long, tedious, and generally conducive to inaccurate results. The volumetric methods, although somewhat better, are unreliable for small amounts of antimony, in part because of a comparatively large and variable blank titration and also because many methods make no provision for the removal of arsenic, which is subsequently titrated quantitatively along with the antimony. With either gravimetric or volumetric analyses the entire result is often accounted for by analytical error alone. A satisfactory method must not only determine antimony when present but also refrain from finding it when none exists.

Experimental

A method involving the decomposition of antimonial solder in hot concentrated hydrochloric acid was first investigated. The significant fact was noted that pure tin-lead solder remains inert and apparently unattacked for long periods in boiling hydrochloric acid, while solder containing as little as 0.01 per cent of antimony is immediately attacked by boiling hydrochloric acid with resultant solution of the tin and lead and precipitation of the antimony in the form of voluminous black flakes.

Andrews (*2*) and Yockey (*6*) proposed methods which involved treatment of the alloy in hydrochloric acid and potassium iodide, followed by recovery of the precipitated metal by filtration and washing. However, the freshly precipitated voluminous metal dissolves on the filter paper on washing with water. In a number of tests the entire black precipitate was observed to disappear completely, giving a clear filtrate. This may be accounted for on the theory that the voluminous precipitate adsorbs tremendous proportions of hydrochloric acid which is capable of dissolving the metal when the latter is exposed to the oxidizing influence of the air.

Nevertheless, an empirical method based on the decomposition of antimonial solder in hot hydrochloric acid was developed. First, a large test tube was drawn out to a fine capillary at one end in such manner that a sample of decomposed antimonial solder, together with the acid, could be poured directly into the tube and the antimony allowed to settle out in the capillary portion, after which the length of the column of precipitated metal could be measured. It was found convenient to set the tube, with capillary end down, into a buret clamped upright and use the buret graduations to secure an empirical reading. The tube was then calibrated by digesting in turn a number of prepared alloys of known antimonial content and noting the reading in each case. By plotting these readings against known antimonial contents, a curve was obtained by means of which an unknown alloy could be investigated. This method was found unreliable for alloys containing bismuth, which is precipitated to some extent along with the antimony. For alloys containing as much antimony as bismuth no measurable error is introduced, but when the bismuth content reaches five times that of the antimony an error of 100 per cent may result. Nevertheless, for certain control analyses in which the solder is known to be free from bismuth or where it is desired to know whether the antimony is above a given maximum, the method is fast and reliable. It depends for its success on an exact duplication of technic.

Of all the available methods of antimony determination, the potassium permanganate, modified after Low (*4*), and the potassium bromate, modified after Györy (*3*) and Rowell (*5*), are most used. The further investigation of these methods was directed towards the elimination of the high variable blank titration which one secures even when antimony is not present. For this work pure solder (containing approximately 0.003 per cent of antimony and 0.01 per cent of arsenic) was used as the sample.

That the solder used was practically free from antimony was established in the following way:

Three of the 150-gram samples of pure solder previously mentioned were converted to 0.01, 0.02, and 0.03 per cent antimonial alloys, respectively, by the addition of the theoretical amounts of antimony; a fourth sample used in the test was not altered. One gram of sawings was then taken from each sample, placed in 250-cc. covered beakers with 75 cc. of concentrated hydrochloric acid, and boiled. The 0.03 per cent antimonial alloy went completely into solution (with the exception of a few black flakes of precipitated antimony) in 8 minutes, the 0.02 per cent in 11 minutes, and the 0.01 per cent in 15 minutes; the pure sample required 95 minutes of alternate boiling and digestion on the steam bath to effect solution. A quantitative investigation was then made by digesting 5-gram samples of the three antimonial alloys and making a curve as previously described. This slightly hyperbolic curve was extrapolated to the axis. A 5-gram sample of pure solder was then digested, the reading referred to the extrapolated portion of the curve, and the corresponding maximum antimonial content noted.

This analysis is, of course, open to the theoretical objection that it was necessary to assume the exact shape of the curve

at the extreme end, and that some antimony may have gone into solution in the course of the long boiling and digestion; however, the fact that the addition of antimony to the extent of 0.01 per cent produces such a marked change in behavior indicates that the sample originally did not contain this metal in amounts approximating this figure.

An attempt was first made to decompose a 1-gram sample of solder in concentrated sulfuric acid and, after the addition of hydrochloric acid and water, to boil and cool the mixture and then titrate direct with 0.05 *N* potassium permanganate as recommended in a number of standard methods. This procedure was found wholly unsatisfactory, as large volumes of potassium permanganate were consumed in the titration and a sharp end point could not be secured. A fairly sharp end point was obtained by first filtering off the precipitated lead sulfate, but there was still a blank titration of 0.6 to 0.8 cc. of 0.05 *N* potassium permanganate which, on the basis of the 1-gram sample used, would correspond to 0.18 to 0.24 per cent of antimony. A still higher blank titration was obtained by the potassium bromate method, modified by decomposing the 1-gram sample with hot sulfuric acid, adding water and hydrochloric acid, heating the mixture until all was in solution, and then titrating hot, using methyl orange indicator. However, the blank was reduced somewhat by prolonged boiling before titrating.

The regular potassium bromate method, involving treatment with hydrochloric acid and bromine followed by reduction with sodium sulfite, did not prove satisfactory for solder, owing to the precipitation of lead sulfite and the formation of a cloudy mixture which did not give a sharp end point.

No particular advantage could be gained by using a 5-gram sample (and increasingly more reagent) instead of 1 gram, as with either the modified bromate or the permanganate method the amount of blank titration is somewhat in proportion to the amount of reagent used. It was therefore decided that one requirement in the solution of this problem lay in keeping the amount of reagents as low as possible and that a certain amount of blank, apparently due to chemicals, was unavoidable.

After some experimentation involving judicious choice of apparatus, it was found that a 2-gram sample could be satisfactorily analyzed with 12 cc. of sulfuric acid, 30 cc. of hydrochloric acid, and 350 cc. of water. The blank titration due to these reagents alone is 0.20 cc. of 0.05 *N* potassium permanganate and must be subtracted from the total titration in making an analysis.

Since arsenic is titrated quantitatively by potassium permanganate in dilute acid solution after digestion with sulfuric acid, it must be removed completely before titrating for antimony. This is accomplished by boiling for a few minutes with a little water and hydrochloric acid after digestion with sulfuric acid, very much as recommended by the American Society for Testing Materials (*1*).

A method was finally developed in which the end point is sharp and distinct and can be determined accurately to a drop of 0.05 *N* solution. The method is fast and its high order of precision is indicated by reference to Table II. No antimony would be reported in an alloy which contained none.

Repeated analyses of pure solder (0.003 per cent of antimony and 0.01 per cent of arsenic) gave consistently a titration of 0.20 cc. of 0.05 *N* potassium permanganate, which is the blank on the reagents. A 0.21 per cent arsenic alloy, made by adding the theoretical amount of arsenic to a sample of pure solder, was also analyzed with the same result, proving the arsenic to have no effect on the titration. Both alloys (0.01 and 0.21 per cent of arsenic) were then analyzed as before, except that the step for the removal of arsenic was omitted, analyses of 0.01 and 0.21 per cent of arsenic, respectively, were obtained.

Table II. Determination of Antimony by Proposed Method

Known Antimonial Content	Antimonial Content Found
%	%
0.03	0.04
	0.04
	0.03
	0.04
	0.04
	0.03
	0.04
	0.04
	0.03
	0.03
	0.03
0.05	0.06
	0.06
	0.05
	0.06
1.00	0.98
	0.98
	0.98
	0.99
	0.99
	1.00
2.00	1.98
	1.99
	1.99
	1.99

Method

Make a preliminary qualitative test for antimony by treating 1 gram of filings in a covered 250-cc. beaker with 50 cc. of concentrated hydrochloric acid and gently boiling the acid. If the metal is immediately attacked by the acid with the liberation of small, fine bubbles of gas, and visual disintegration of the sample, antimony is present. If after 10 minutes' boiling there is no visual indication that the acid is attacking the metal and the sawings appear to lie inert in the bottom of the beaker in large aggregates formed from the coalescence of small adhering particles, antimony is not present and the analysis may be discontinued. The presence of 0.01 per cent of antimony in solder readily manifests itself in altering the behavior of the metal in boiling hydrochloric acid.

Having demonstrated that antimony is present, weigh 2 grams of sawings into a loosely covered 250-cc. extraction flask, add 12 cc. of concentrated sulfuric acid, place the flask on a piece of perforated asbestos, and heat over a free flame until decomposition is complete and the precipitated lead sulfate is white; then continue to boil gently for a few minutes longer, occasionally shaking the flask. (A small, porcelain crucible, placed upright, makes a very convenient cover for the flask.) Allow the mixture to cool, add cautiously 15 cc. of water and then 15 cc. of hydrochloric acid, and boil for 10 minutes to expel arsenic. To the boiling solution add 50 cc. of water and 15 cc. of hydrochloric acid and continue to boil for a few minutes longer to insure the complete solution of antimony sulfate. Any insoluble residue consisting of small amounts of lead sulfate and particles of free sulfur may be ignored. Cool the flask thoroughly in running cold water and filter by suction through a No. 3 Büchner funnel, washing once by decantation and two or three times more on the filter with 10-cc. portions of sulfuric acid (1 to 10). Transfer the filtrate to a beaker, dilute to 400 cc. with water which has been cooled to approximately 10° C., and titrate slowly at 15° C. with 0.05 *N* potassium permanganate until the pink color tends to persist. The filtration should be done rapidly and the titration made promptly, as there is an additional precipitate of the lead salt on standing. A titration of 0.20 cc., due to a blank determination on reagents treated under the same conditions, must be subtracted from the total titration.

$$\text{Titration} \times \text{normality} \times 3.04 = \text{per cent of antimony}$$

Notes on the Analysis

The extraction flask recommended for the digestion of the alloy is a special type of Erlenmeyer which stands about 16 cm. high and measures about 7 cm. across the bottom. Such a flask has the advantage that a large amount of sample can be treated with a relatively small amount of reagent.

A considerable amount of sulfur separates out during the digestion; this does not affect the results.

Obviously an application of this method leads to the

determination of arsenic. By subtracting the titration secured in the determination of antimony from the titration resulting from an analysis in which arsenic is not removed, one can secure a titration due to arsenic alone. Equal amounts of reagent, however, should be used.

The pink color fades rapidly at the end point; the latter is reached when, on the addition of a drop of permanganate, the color does not fade instantly but tends to persist.

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Detection of Calcium in the Presence of Strontium and Barium

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While it has long been known that calcium hydroxide is more insoluble than either strontium or barium hydroxide, especially at temperatures near the boiling point of water, this fact has not found practical application as the basis of a qualitative precipitation reaction for calcium, owing to the usual carbonate content of alkali hydroxide solutions applicable as reagents. However, if hydroxyl ions are generated by the interaction of mercuric oxide and potassium iodide within a solution to be tested for calcium, under conditions that exclude the presence of any carbonate ion, the slight solubility of calcium hydroxide may be safely utilized for the detection of calcium in the presence of the other two alkaline earth ions. The reaction involved in this method can be represented by the equation:

$$CaCl_2 + HgO + 4KI + H_2O \longrightarrow Ca(OH)_2 + 2KCl + K_2HgI_4$$

In practice a chloride solution known to contain only alkaline earth salts is reduced to small volume, rendered slightly acid with hydrochloric acid, and transferred to a test tube. The solution is boiled for a few minutes to expel all carbon dioxide, and while still actively boiling a suitable quantity of solid potassium iodide is added. When this has dissolved, powdered mercuric oxide is added to the continuously boiling solution, and if a white cloudy precipitate appears as the mercuric oxide rapidly dissolves, the presence of calcium is indicated. This simple technic effectively excludes carbon dioxide and at the same time takes advantage of the fact that the solubility of calcium hydroxide is at its minimum at this temperature, whereas the solubilities of the other two alkaline earth hydroxides are at their maxima.

Materials and Apparatus

Both reagents required for this test must be free from sulfates and from metals that can be precipitated as hydroxides, including calcium itself. In addition, a blank made with the quantities of potassium iodide and mercuric oxide used in the test should give a clear solution. Yellow mercuric oxide is to be preferred to the red form, since its smaller particle size leads to more rapid and complete solution during the reaction with potassium iodide, and furthermore, the precipitated form can usually be obtained in a higher state of purity. The usual laboratory grade of potassium iodide was found suitable.

Preliminary experiments showed that the necessary complete and rapid solution of the mercuric oxide in convenient volumes of test solution occurred only when the weight of the potassium iodide approached ten times that of the oxide. Attempts to use an already prepared mixture of the two reagents were not successful, since the intimately mixed solids, even when carefully dried, reacted with each other and absorbed carbon dioxide from the air on standing a comparatively short time.

The standard calcium solution, containing 0.0010 gram of calcium per cc., was prepared by dissolving 2.4970 grams of pure calcium carbonate in the minimum necessary quantity of hydrochloric acid, boiling to expel all carbon dioxide, and cooling, and finally adjusting the volume to 1000 cc. The concentration of this solution was checked by igniting and weighing the calcium sulfate obtained by the evaporation of 100.0 cc. with a slight excess sulfuric acid in a platinum dish.

Because the ordinary c. p. grades of barium and strontium chlorides were found unsuitable by reason of their calcium content, barium chloride dihydrate and strontium chloride hexahydrate included in DeHaen's line of specially purified reagents were employed. These salts were stated to contain not more than 0.0005 and 0.01 per cent of calcium, respectively. Instead of using standard solutions, it was found more convenient to take weighed quantities of these salts, thus avoiding numerous evaporations.

The test experiments were made in graduated hard-glass test tubes, generally used in pairs in order to compare a given sample directly with a blank or with another sample containing a smaller or a larger amount of calcium. These tubes were mounted upright so that the solid reagents could be dropped in without loss from adhesion to the sides. To promote smooth boiling in this position, when using ordinary gas burners, it was found necessary to place small spirals of platinum wire in the test solutions.

Experiments

Where calcium was present alone (Table I), the necessary volumes of standard calcium solution were first pipetted into the graduated test tubes and acidified with one drop of 0.1 *N* hydrochloric acid. The solutions were next adjusted with distilled water to slightly more than the desired final volume in each case, and boiled down to the given fixed volume before adding the potassium iodide. Where the quantity of potassium iodide was large enough to make a significant difference in volume, the solutions were again boiled to the desired final volume before adding the mercuric oxide. The period of observation for judging the absence or presence of any cloudiness or turbidity, due to precipitated calcium hydroxide, was restricted to about a minute after the addition of the mercuric oxide in order to avoid error due to the decreasing volume of the continually boiling solution. In all cases where a precipitate was observed, the fact of its being calcium hydroxide, and not calcium carbonate due to carbon dioxide from the air, was confirmed by diluting the mixtures

with cold recently boiled water and noticing the clearing effect from the redissolving of all or most of the precipitate. The need for using a restricted volume of solution together with a sufficient quantity of reagents is evident. Under these conditions the test is fairly sensitive, perhaps more so than would be expected. The decreased solubility shown by calcium hydroxide in this case is no doubt due to the combined effect of high temperature and a comparatively high concentration of hydroxyl ion. Saturated calcium sulfate solution also gave a copious precipitate when subjected to this test.

Table I. Results with Calcium Present Only

Final Solution Volume	Potassium Iodide Added	Mercuric Oxide Added	Reaction Observed with Given Amount of Calcium			
			0.2 mg.	0.5 mg.	1.0 mg.	2.0 mg.
Cc.	*Grams*	*Gram*				
2	0.10	0.01	−	−	+	+
2	0.20	0.02	−	+	+	+
2	0.30	0.03	+	+	+	+
2	0.50	0.05	+	+	+	+
5	0.30	0.03	−	−	−	+
5	0.50	0.05	−	−	+	+
5	0.70	0.07	−	+	+	+
5	1.00	0.10	−	+	+	+
10	0.50	0.05	−	−	−	−
10	1.00	0.10	−	−	−	+
10	1.50	0.15	−	−	+	+
10	2.00	0.20	−	−	+	+

Table II. Effect of Strontium and Barium

Barium Present	Strontium Present	Reaction Observed with Given Amount of Calcium			
		0.0 mg.	0.5 mg.	1.0 mg.	2.0 mg.
Mg.	*Mg.*				
100	0	−	+	+	+
200	0	−	+	+	+
300	0	−	+	+	+
400	0	−	−	+	+
500	0	−	−	+	+
0	100	−	+	+	+
0	200	−	−	+	+
0	300	−	−	+	+
0	400	−	−	−	+
0	500	−	−	−	+
50	50	−	+	+	+
100	100	−	−	+	+
150	150	−	−	+	+
200	200	−	−	+	+
250	250	−	−	−	+
300	300	−	−	−	+
100	50	−	+	+	+
200	50	−	−	+	+
400	50	−	−	+	+
50	100	−	+	+	+
50	200	−	−	+	+
50	400	−	−	−	+

In Table II will be seen the results of experiments on detecting calcium in the presence of strontium and barium. In these trials the proper amounts of alkaline earth chlorides were first weighed into the graduated tubes and dissolved in small volumes of water, and the procedure described above was followed. In all these cases, however, a fixed volume of 5 cc. was used, and 1.00 and 0.10 gram, respectively, of potassium iodide and mercuric oxide were added. While in no case were reactions obtained with strontium or barium solutions alone, the presence of these other ions in high concentrations tended to decrease slightly the sensitivity of this test for calcium, the effect being more marked in the case of strontium than barium. This is shown not only by the trials where but one is present in addition to calcium, but also by the results on solutions containing various proportions of all three alkaline earth ions. This impairment of sensitivity, however, is not so great as to interfere much with the practical value of the test, for only in extreme cases were negative results obtained when 1 mg. of calcium was present. In general the experiments indicate that within the alkaline earth group this method for the detection of calcium is apparently more specific than any previously suggested chemical test.

Interfering Substances

Because of their reactions with mercury compounds and their effect on the solubility of calcium hydroxide, ammonium salts interfere seriously and must be removed completely. Anions of high oxidizing power, such as chromate ion, cannot be present because of their reaction with iodide ion, but the test can be made in the presence of nitrate ion. All other cations precipitable as hydroxides must be absent. With the exception of magnesium these are easily removable by the usual sulfide procedures prior to applying the test. Several different ways for separating from magnesium were tried, in particular repeated carbonate and oxalate precipitations, the final alkaline earth precipitate being dissolved in a small volume of dilute hydrochloric acid for the test. These were not found satisfactory, chiefly because enough magnesium accompanied the alkaline earths on single precipitation to interfere in the test, while its complete separation by double or triple precipitation caused too much loss of calcium. It was also difficult to obtain any precipitate with small amounts of calcium in the presence of several hundred times as much magnesium. On this account a special method was devised, based upon the ignition of the mixed carbonates of the alkaline earths and magnesium followed by aqueous extraction of the ignited residue. By this treatment any magnesium present is converted to oxide along with the calcium and some strontium, but the magnesium oxide by reason of its low solubility is not dissolved in appreciable amount by extraction with a small volume of cold water. This method is incorporated in the following general procedure for the rapid separation of calcium from a solution that may contain any of the cations.

General Procedure

After removing all heavy metals by sulfide precipitations, the final filtrate is evaporated to a volume of 10 to 15 cc., any free sulfur being removed by filtration. About 25 cc. of 6 *N* ammonium carbonate solution are now added, together with an equal volume of 95 per cent ethyl alcohol. The mixture is allowed to stand for about 30 minutes with frequent stirring, after which the precipitate is filtered off on an ashless paper. After two or three washings with 50 per cent ethyl alcohol, the precipitate and filter are dried rapidly by suction and transferred to a platinum crucible for ignition at about 900° C. for 15 to 20 minutes. The ignited mass is allowed to cool in the crucible with cover on, and if the residue appears lumpy it is rapidly ground in a mortar before transferring it to a 25-cc. flask or test tube. This vessel is then filled with cold recently boiled water, stoppered, and allowed to stand with frequent shaking about 30 minutes, after which the residue is filtered off. The filtrate is rendered just slightly acid with hydrochloric acid before being rapidly evaporated to a volume of not more than 5 cc. It is finally transferred to a test tube containing a platinum wire spiral or other device to prevent bumping. About 1.0 gram of potassium iodide is then added and the liquid is boiled continuously as this dissolves. Finally, about 0.10 gram of yellow mercuric oxide is added to the boiling solution. As this dissolves the formation of a cloudy white precipitate is indicative of the presence of calcium.

This procedure gave negative results when tested on pure magnesium solutions that were prepared by dissolving known weights of vacuum-distilled metallic magnesium in the minimum necessary amount of dilute hydrochloric acid. On the other hand, positive tests were obtained on solutions containing 500 mg. of magnesium to which 1.0 mg. of calcium had been added. Positive results were likewise obtained with solutions containing 1.0 mg. of calcium and a total of 500 mg. of magnesium, strontium, and barium in various proportions.

The use of a platinum crucible is recommended, since attack of the glaze of a porcelain crucible during ignition sometimes leads to a slight precipitation in samples supposed to contain no calcium. The stated temperature should not be exceeded when barium or strontium is liable to be present in large proportion, on account of the fusibility of their carbonates. For rapid qualitative work, where no semi-quantitative comparisons are to be made, it is sufficient to measure

out the solid reagents by volume from a spoon or spatula instead of by weight.

Practical Applications

While this test is capable of general qualitative use and even of incorporation in the usual qualitative scheme, it appears especially suited for the detection of calcium in nearly pure barium or strontium salts, where interference from magnesium is negligible, for purposes of analytical research or manufacturing control. Here it can be applied in a semiquantitative way, by testing a series of progressively smaller or larger samples until a negative or positive reaction is obtained, reference being made to previously established behavior of known concentrations of calcium in solutions whose concentration in respect to the particular barium or strontium salt is identical to that of the unknown test solution. In making such comparisons the volumes of the solutions, the weights of reagents, and the time of observation must be the same. This scheme was found to be more practical than the usual method of comparison, since the nature of the test interferes with the convenient use of a series of turbidity standards.

The feasibility of this procedure was tested on a representative specimen of c. p. strontium chloride. The test apparently possesses sufficient accuracy to determine whether or not the percentage of calcium present as an impurity is below or above a desired limit, and since it involves no preliminary separations it has the advantage of yielding rapid results.

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Pure Titanium Oxide as a Standard in the Volumetric Estimation of Titanium

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TITANIUM oxide in titanium pigments or other titanium-containing materials may be estimated by a volumetric method involving reduction of the titanium in solution and titration with a ferric salt (*5*, *7*). A rapid and entirely satisfactory procedure for this estimation has been recently described (*3*).

Standardized ferric ammonium sulfate solution is used in the titration of the reduced titanium solution, and is of such concentration that 1 ml. is equivalent to 0.005 gram of titanium dioxide. This solution is standardized by reduction and titration with 0.1 *N* potassium permanganate, which in turn has been standardized against sodium oxalate. [The ferric ammonium sulfate is prepared by dissolving 30 grams of the salt in 300 cc. of distilled water acidified with 10 cc. of sulfuric acid. Potassium permanganate solution is added drop by drop as long as the pink color disappears. The solution is finally diluted to 1 liter. In standardizing, 50 ml. of the solution are made up to about 100 cc. in 5 per cent sulfuric acid, reduced in a Jones reductor (*4*) and titrated against standard 0.1 *N* potassium permanganate.]

The authors have found it convenient to prepare pure titanium dioxide as a known sample to check the operation of their reductors and the standardization of the ferric ammonium sulfate solution. Since a zinc amalgam reductor loses its efficiency after considerable use, it is advisable occasionally to check its operation by running a known sample, and for this purpose pure titanium oxide is most suitable. In laboratories which analyze for titanium as a matter of routine but have little other occasion to use a standardized potassium permanganate solution, pure titanium oxide might be an excellent means of standardizing ferric ammonium sulfate solution.

About 0.2 gram of the pure oxide is weighed accurately into a 250-cc. beaker, 20 to 30 cc. of sulfuric acid and 10 grams of ammonium sulfate are added, and the mixture is carefully boiled until the titanium oxide is dissolved. After cooling, the contents are diluted to 125 to 150 cc., reduced in the usual manner in a Jones reductor, and titrated (ammonium thiocyanate indicator) with the ferric ammonium sulfate solution to be standardized. In this way the preparation and standardization of a potassium permanganate solution, and any attendant errors are avoided.

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Certain Bureau of Standards chemists (*1*) have shown that the results obtained for titanium dioxide in Titanox by following Barton's modification (*7*) of the Shimer method (*6*) are a little too low, owing, presumably, to the slight oxidation of the titanous sulfate at the expense of atmospheric oxygen. This being the case, the proposed empirical standardization process will lead to more accurate values than can be obtained by working through a potassium permanganate solution whose titer has been otherwise set because a compensation of errors occurs.

Preparation of Pure Titanium Oxide

Pure titanium oxide is prepared by a modification of a previously published method (*2*):

Crude titanium tetrachloride is distilled, collecting the 135° to 138° C. fraction, in the presence of an excess of chlorine to prevent the distillation of iron compounds with the titanium tetrachloride. The authors have found it advantageous to pack joints in the distillation apparatus with glass wool instead of using corks or stoppers.

The distilled titanium tetrachloride is dissolved by pouring 500 cc. in small portions into 1500 cc. of distilled water with vigorous stirring. The mixing beaker should be immersed in a cold water bath and the operation carried out under a hood, using rubber gloves. (Titanium tetrachloride may be poured upon clean ice instead of into distilled water with much less attendant fuming, the weight of the ice in grams being equal to the volume of the water in cubic centimeters.) A clear solution containing about 15 per cent titanium oxide is obtained. This is reduced electrolytically or by means of stick zinc to about 0.5 gram per liter of reduced titanium oxide, and 100 cc. are further reduced to about 3 grams per liter of reduced titanium oxide. The solution is reduced until distinctly colored by the presence of titanous ion; all the iron present must be in the ferrous state to prevent hydrolysis and precipitation of ferric iron with the titanium. Dilute oxalic acid also prevents precipitation of any iron with the titanium. The highly reduced titanium tetrachloride solution is added drop by drop to a boiling solution of 5 grams of oxalic acid in 3500 cc. of water contained in a round-bottomed flask. Then 400 cc. of the lightly reduced solution are added dropwise, over a period of 1 hour, and boiling is continued thereafter under reflux for half an hour. The precipitation yield will be about 99 per cent. The precipitate is transferred to a 4-liter beaker, allowed to settle, decanted, repulped (brought back into suspension) with about 20 cc. of concentrated sulfuric acid per 4 liters, filtered, and washed with hot distilled water until the washings are free from chloride.

The hydrous titanium oxide so obtained is dehydrated to form pure titanium dioxide by igniting at about 900° C.

A spectroscopic analysis (by E. Posnjak, Geophysical Laboratory, Carnegie Institution, Washington, D. C.) of titanium oxide prepared as above showed the presence of 0.001 to 0.01 per cent of sodium as the only impurity. This last is probably due to contamination during the handling of the calcined titanium dioxide, as no special care was observed in order to obtain a spectroscopically pure product.

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Inclusion of Rarer Metals in Elementary Qualitative Analysis

II. Inclusion of Titanium and Vanadium in Group III

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THE detection of tungsten and molybdenum in the presence of the common ions of groups I and II has been described in a previous paper (*3*). The detection of the only other two rarer metals to be considered in this series is outlined in the present paper.

Solutions of titanium salts may be prepared by fusion of titanium dioxide with an excess of sodium bisulfate, followed by solution in water and acid. To remove the sulfate ion, the titanium is precipitated as the hydroxide by means of ammonium hydroxide, and the filtered and washed precipitate is dissolved in dilute hydrochloric or nitric acid and diluted to the desired volume. An alternative method is fusion of the oxide with sodium peroxide, followed by extraction with water and decomposition of the peroxide with acid and sodium sulfite. Vanadium may be conveniently used in the form of sodium vanadate which is readily soluble in water. Since vanadates precipitate in group III only in the presence of other members of the group, it is essential that at least one such metal be present when testing for vanadate.

The filtrate from group II is treated with hydrogen sulfide in the presence of ammonium chloride and ammonium hydroxide in the usual manner. A little more ammonium hydroxide should be added before filtration, in order to overcome the possible formation of soluble ammonium sulfovanadate. After filtering off the group III precipitate, the filtrate should be acidified with acetic acid and boiled to remove hydrogen sulfide. A brownish precipitate containing some of the vanadium may be formed at this point, and should be filtered off and added to the precipitate of group III. The solution will contain groups IV and V.

The entire precipitate of the group is suspended in 50 cc. of *N* hydrochloric acid, and the mixture is thoroughly stirred, allowed to stand from 3 to 5 minutes, and filtered. The residue may contain the sulfides of nickel and cobalt. The filtrate is evaporated to about half its original volume to remove hydrogen sulfide and part of the mineral acid. It is then made neutral with 5 *N* or 6 *N* sodium hydroxide, and 10 cc. of sodium hydroxide are added in excess, together with 10 cc. of 3 per cent hydrogen peroxide. Sodium peroxide may be substituted here if desired. The mixture is boiled for at least 5 minutes to decompose the excess of peroxide and insure the complete precipitation of the titanium. After being cooled, the mixture is filtered to separate the iron division from the aluminum division.

DETECTION OF TITANIUM IN THE IRON DIVISION

The precipitate may contain ferric hydroxide, titanium hydroxide, and manganese dioxide. A common method for the separation of these with other metals includes the precipitation of the manganese by boiling with potassium chlorate and nitric acid, but this is not advisable in the hands of a large class because of the acid fumes that are evolved and because under these conditions much of the titanium may be precipitated with the manganese (*2*). Furthermore, ammonium hydroxide and ammonium chloride cannot be used to precipitate the iron and titanium from the manganese because some or all of the manganese will precipitate with the titanium.

The residue of these three metals is therefore dissolved in hot dilute nitric acid, with the addition of 1 or 2 drops of hydrogen peroxide if necessary to effect solution. The excess hydrogen peroxide must be removed by boiling. The cooled solution is made neutral with ammonium hydroxide and a slight excess of dilute nitric acid is added to decompose any hydroxides that may be present. To this solution a suspension of barium carbonate in water is added until an excess remains undissolved. Upon standing for at least 3 minutes with occasional stirring, the excess of nitric acid is neutralized by dissolving some of the barium carbonate, and the hydrogen-ion concentration in the resulting solution is such that all of the iron and titanium is completely precipitated as hydroxides while the manganese is left in solution. The use of a soluble base in place of the barium carbonate would result in the precipitation of part or all of the manganese. After filtration the lead dioxide test for manganese is made. The residue, including some excess barium carbonate along with the titanium and iron, is dissolved in dilute hydrochloric acid, and, after the addition of 1 gram of ammonium chloride, the titanium and iron are precipitated by an excess of ammonium hydroxide. The precipitate is filtered off to remove the soluble barium salts which would interfere with later tests. The residual hydroxides of titanium and iron may be dissolved in hydrochloric acid and the iron extracted with ether (*2*).

Ether extraction may be avoided by making use of the fact that titanium phosphate will not be precipitated in the presence of an excess of hydrogen peroxide (*1*). The hydroxides of the two metals are dissolved in dilute sulfuric acid. To this are added 5 cc. of hydrogen peroxide, some sodium hydrogen phosphate, and an excess of sodium hydroxide. The residue of ferric hydroxide and ferric phosphate is filtered off and the test for iron made in the usual manner. The filtrate is made slightly acid with dilute sulfuric acid, the formation of a yellow or orange solution at this point indicating the presence of titanium, and is then treated with sodium sulfite and a little more phosphate and warmed. After the reduction of the peroxide, the formation of a white precipitate of $TiOHPO_4$ proves the presence of titanium. If the solution is too strongly acid for this precipitate to form, it should be neutralized with sodium hydroxide.

Detection of Vanadium in the Aluminum Division

The filtrate from the treatment with sodium hydroxide and sodium peroxide may contain sodium chromate, vanadate, aluminate, and zincate.

If it is just acidified with dilute nitric acid (1 to 3) and an excess of 3 cc. of acid are added for each 50 cc. of solution, the chromate may be removed as the lead salt upon the addition of an excess of lead nitrate. After filtration, the presence of chromium is confirmed by the use of nitric acid and hydrogen peroxide. If to the filtrate 1 or 2 grams of ammonium acetate are added, the pH will be sufficiently increased to cause complete precipitation of the vanadium as $Pb_3(VO_4)_2$. As little as 0.5 mg. of vanadium may be detected in this way after the removal of the equivalent of 50 mg. of potassium chromate as the lead salt. The lead vanadate is filtered off and washed thoroughly to remove soluble lead salts, which would otherwise interfere with the end test for vanadium. Three or four drops of dilute ammonium hydroxide are poured over the lead vanadate on the paper and washed through with 5 cc. of water. This solution is then saturated with hydrogen sulfide to yield a red solution of ammonium sulfovanadate, $(NH_4)_3VS_4$, if vanadium is present. The filtrate from the lead vanadate is treated with 3 or 4 cc. of 3 *N* hydrochloric acid, and the excess of lead is precipitated by the use of hydrogen sulfide. The lead sulfide is filtered off and washed with 5 or 10 cc. of *N* hydrochloric acid to dissolve any zinc sulfide that may have been precipitated because of the presence of the ammonium acetate. After the removal of the sulfide by boiling, the aluminum is separated by ammonium hydroxide, and the zinc is detected in the filtrate by the use of hydrogen sulfide.

Solutions which may contain tungsten, molybdenum, titanium, and vanadium in addition to the common metal ions have been issued to the author's students as unknowns near the end of a semester course in elementary qualitative analysis, with satisfactory results. Not only do the students appear interested in the direct contact with these metals, which they recognize as of considerable commercial importance, but they are introduced to many of their properties, including several oxidation and reduction reactions with their several striking color changes. There is also ample opportunity for class discussion of the theory involved, such as the influence of hydrogen-ion concentration in making possible the separation of chromate and vanadate as the lead salts.

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Potentiometric Titration in Nonaqueous Solutions

II. A Source of Error in Acidimetry

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In acidimetry in alcoholic solution a weak acid, resulting from oxidation of the alkali solution, may be introduced into the system as the alkali salt. A simple quantitative test for the presence of impurities, in the form of weak acid salts or weak bases, in the alkali solution may be made by titrating portions of standard picric acid.

In acidimetry in butyl or amyl alcohol solution, using as reagent an alkali metal hydroxide in the same solvent, several workers have reported the appearance of anomalous points of inflection on the titration curves (or maxima on the $\Delta E/\Delta V$ curves) of both used oils and single monobasic acids (*2*, *3*). Recently, in titrating picric, trichloroacetic, and dichloroacetic acids in butyl alcohol solution the authors have obtained similar titration curves (Figure 1). The appearance of two inflection points on the titration curve of a monobasic acid can be attributed only to the presence, as an impurity, of a considerably weaker or stronger acid than the one being titrated. A systematic search for the source of this impurity has led to conclusions which are of general importance in connection with the use of alcoholic solutions for precise acidimetry.

Apparatus

The apparatus used consisted of a thermionic titrometer, an electrode system, a titration cell, and a storage system for alkali solution such as those previously described (*1*).

The collection of the data in this paper was facilitated by the use of the thermionic titrometer, by which the slope of the titration curve is read directly. This instrument also made possible the elimination of neutral salts such as lithium chloride, which have heretofore been used to reduce the resistance of butyl alcohol solutions (*4*, *5*).

Reagents

Alkali Solution. A solution of potassium hydroxide in *n*-butyl alcohol (0.05 *N*), prepared and stored as described in the former paper (*1*), was used as a standard reagent in most of the work reported. The solvent was purified as described previously, except that the distillations were carried out at reduced pressure (30 to 40 mm. of mercury), and barium oxide was substituted for calcium oxide as a dehydrating agent.

The use, in the latter part of this work, of sodium butoxide as an acidimetric reagent was found to offer several advantages over potassium or sodium hydroxide. This reagent, prepared by the interaction of metallic sodium and pure *n*-butyl alcohol in a reducing atmosphere, is carbonate-free and is reasonably stable if properly protected from light and the atmosphere. This may be conveniently accomplished by storing under hydrogen in a light-proof bottle.

Deterioration of the alkali solution is indicated by a decrease in neutralizing value in terms of benzoic acid, which is accompanied as the solution ages by the appearance of a yellow color and a slight turbidity. A quantitative test for the purity of the alkali reagent is described in the last section of this paper.

Quinhydrone. The quinhydrone used in most of the work was obtained from the Eastman Kodak Company. Recrystallization from butyl alcohol did not perceptibly improve its quality. Quinhydrone prepared by the method of Valeur (*7*) was used in a few titrations. The quinhydrone was stored in a dark bottle and was dissolved immediately before use.

Solvent. The solvent employed in most of the work was the practical grade of *n*-butyl alcohol supplied by the Eastman Kodak Company, used both with and without further purification. The method of purification employed was distillation at reduced pressure from barium oxide.

Blank on Reagents. The value of the blank titration on 100 cc. of solvent containing 50 mg. of quinhydrone usually was found to be 0.05 cc. or less of 0.05 *N* alkali solution. If the blank exceeded this value the solvent was redistilled as described above.

Acids. Picric acid was obtained from both the Eastman Kodak Company and Merck & Co. Recrystallization from butyl alcohol did not effect any improvement in quality. Solutions of picric acid in *n*-butyl alcohol were found to be very stable, no change in acid value being observed over a period of several months.

The other acids were obtained from the Eastman Kodak Company and were used without further purification.

Experimental

Experiments summarized below were designed to test each of the following possible sources of an acid impurity: the butyl alcohol solvent, the quinhydrone, the nitrogen used for stirring, the acid being titrated, and the alkali reagent.

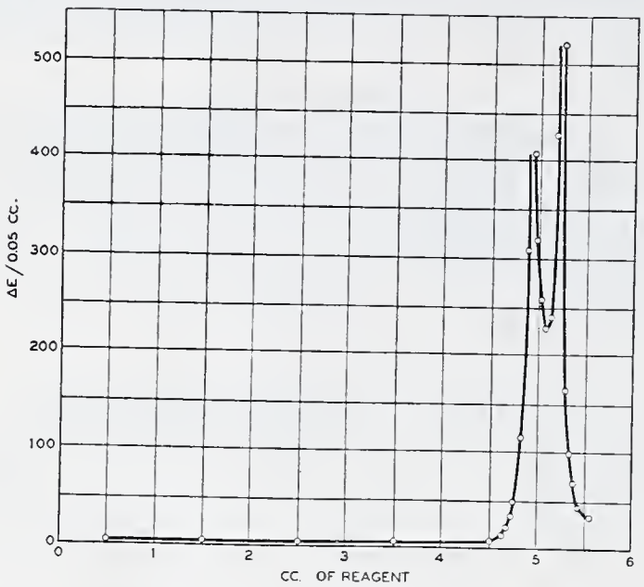

Figure 1. Differential Titration of Picric Acid

Showing anomalous maximum obtained when using an old solution of alkali.

It was found that neither increasing the amount of solvent or quinhydrone used, nor purifying these materials, had any effect on the difference between the first and second maxima. Varying the quantity of nitrogen passed through the solution during a titration was without effect, and the same result was obtained when the nitrogen was carefully purified. Purification of the picric acid used did not eliminate the anomalous maximum, nor did it alter the distance between the two maxima. On the other hand, it was observed that the anomalous maximum on the titration curve occurred only when the alkali reagent was comparatively old; that the distance between the two maxima, for a given titer, increased with the age of the alkali solution; and that the distance between the two maxima was directly proportional to the volume of alkali solution used. The data in Table I show the effect of doubling the quantity of acid titrated, thereby doubling the titer to both the first and second end points. The alkali solution used in these titrations was approximately 2 months old.

Table I. Effect of Doubling Quantity of Acid

Acid Titrated	Titer of 10-cc. Sample 1st	2nd	Diff.	Titer of 20-cc. Sample 1st	2nd	Diff.
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
Picric	4.04	4.60	0.56	8.05	9.18	1.13
Trichloroacetic	4.59	5.27	0.68	9.20	10.67	1.47
Picric[a]	2.73	2.86	0.13	5.50	5.74	0.24

[a] Picric acid from a different source titrated with a different alkali solution.

These experiments eliminated four of the five possible sources of the unknown acid and pointed to the butyl alcohol solution of alkali used as reagent. Further experiments definitely proved that the source of the unknown acid was the alkali reagent. Ten cubic centimeters of an approximately 0.3 *N* butyl alcohol solution of butyric acid were added to 500 cc. of alkali solution which had been freshly prepared and which showed but one maximum in the titration of picric acid. When picric acid was titrated with the alkali thus contaminated, a second maximum appeared (Figure 3-*a*). Addition of a second 10-cc. aliquot of acid to the remainder (384 cc.) of the alkali solution more than doubled the difference between the two maxima when titrating the same quantity of picric acid (Figure 3-*b*). Good agreement, within the estimated experimental error, was obtained between the calculated and the experimentally found increase in titer between the two maxima. A titration of benzoic acid with the contaminated alkali solution yielded but one maximum on the titration curve. These experiments were repeated, employing benzoic and acetic acids as contaminants, with similar results.

Several experiments were performed which indicate how the condition artificially produced above can occur normally. A technical grade of commercial *n*-butyl alcohol was used without purification, for the preparation of an alkali solution. A titration of picric acid with this newly prepared reagent showed two maxima. The same solvent, after purification, was used for an alkali solution which, when titrating picric acid, did not exhibit a second maximum. An alkali solution, which was prepared from pure solvent and which did not give the second maximum when titrating picric acid, was exposed to light and air (protected only from carbon dioxide) for several days. The titration curve of picric acid then revealed two maxima. It was also found that saturating a pure alkali solution with oxygen and then allowing it to stand with no protection from light for 24 hours, would produce a change causing the appearance of a second maximum on the titration curve of picric acid. The fact, repeatedly observed, that an alkali solution, even when prepared from a pure solvent and protected from the atmosphere will, after a period of time, exhibit two maxima when titrating picric acid may therefore be attributed to oxidation of the alcohol, resulting either from leakage of air into the alkali storage system or from the presence of traces of oxygen or other oxidizing agents in the solvent.

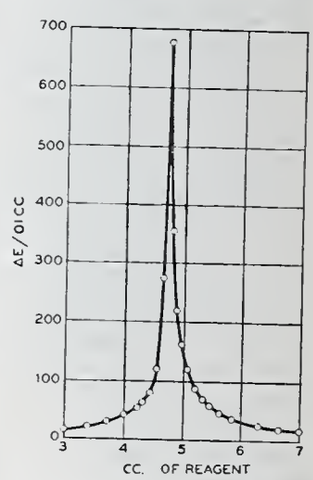

Figure 2. Titration of Picric Acid Using a Pure Solution of Alkali

The strength of the acid resulting from the oxidation of a *n*-butyl alcohol solution of alkali appears to be approximately the same as acetic, since when titrating acids weaker than dichloroacetic only one maximum occurred on the titration curve. This conclusion seems justified in view of the results obtained in titrating mixtures of acetic with each of the chloroacetic acids in *n*-butyl alcohol, using pure alkali solution. Two maxima were obtained in the titration of mixtures of acetic and dichloroacetic while only one maximum occurred in the titration of a similar mixture of acetic and monochloroacetic acids.

The magnitude of the errors resulting from the use of an impure solution is limited by the solubility of the salts of weak acids present. The authors have produced artificially contaminated alkali solutions, employing butyric acid as the contaminant, the use of which could lead to errors in acid values as high as 30 per cent. The use of technical alcohol without purification as the alkali solvent, or storage

of the solution without adequate protection from oxygen, may lead to errors equally as high.

Discussion of Results

The results of the experiments described above show that when titrating a moderately strong acid in *n*-butyl alcohol using an alcoholic solution of alkali, a weak acid may be introduced into the system as the alkali salt; and

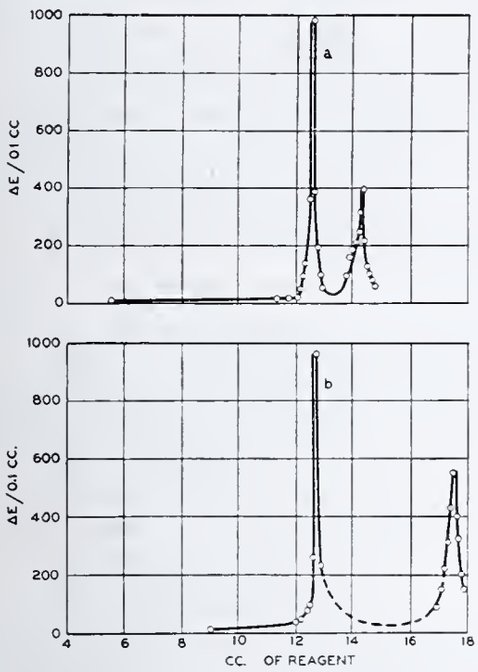

Figure 3. Differential Titration of Picric Acid

a. Using alkali solution contaminated with butyric acid; *b.* Same as *a*, with increased amount of butyric acid.

that the presence of the weak acid salt in the alkali solution probably is associated with the oxidation of the alcohol, or with the oxidation or condensation of aldehydes present as impurities.

An alcoholic solution of alkali thus contaminated may be considered to be a mixture of two bases of different strengths, and the neutralization reaction in the presence of an excess of the strong acid HX may be represented as follows:

$$HX + \begin{cases} NaOR \\ NaA \end{cases} \longrightarrow NaX + HA + ROH$$

Thus the weak acid HA accumulates until the neutralization of the stronger acid HX is completed, and is then itself re-neutralized, causing the appearance of a second maximum on the titration curve. Whether or not the second maximum occurs depends upon the relative strengths of the acids, their relative concentrations, and in a special way upon the solvent (*6*). That conditions are more favorable for the separation of the end points of two acids of different strengths in the solvent *n*-butyl alcohol than in water is shown by Figure 4.

The above equation clearly shows that an alkali solution, contaminated by a weak acid salt, will be weaker in neutralizing power when titrating a weak acid than when titrating a strong one. If benzoic acid is used for standardizing an alkali solution contaminated by the alkali salt of an acid of the same order of strength as benzoic, and subsequently this alkali solution is used for titrating an oil sample which contains a strong acid, the resulting acid value will be in error in the sense of being too low, assuming the first maximum is selected as the correct end point. If the second maximum is used in calculating the acid value, however, the correct result will be obtained, since the weak acid titrated must be exactly the equivalent of the salt used in neutralizing the strong acid originally present in the oil sample. Again, if a mixture of strong and weak acids is present in the sample, the second maximum must be selected to give the correct total acidity. Without presuming a knowledge of the compositions both of the alkali reagent and of the solution being titrated, however, it is impossible to select in every case the end point leading to the correct acid value, when using an alkali solution contaminated by the salts of weak acids. Moreover, one of the maxima may be missed entirely, owing to the limitations of the indicator electrode; or the proximity of the maxima may result in a flat or ill-defined end point. Possibility of error is excluded only if the acid present in the sample is of the same order of strength as benzoic, when only one maximum occurs.

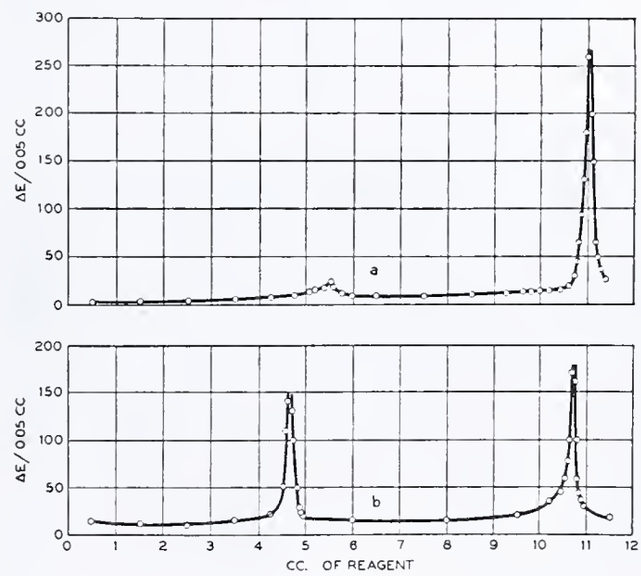

Figure 4. Differential Titration of Mixtures of Trichloroacetic and Acetic Acids

a. In water; *b.* In *n*-butyl alcohol.

It is also clear that no valid conclusions can be drawn as to the presence or absence of mixtures of strong and weak acids in used oils, unless precautions are taken to insure the absence of salts of weak acids from the alkali reagent and to employ a solvent of low blank.

Conclusion

A simple quantitative test for the presence of impurities, in the form of weak acid salts or weak bases, in the alkali solution may be made by titrating portions of standard picric acid solution, carrying the titrations as far as possible into the alkaline region. The sensitivity of the test is determined by the quantity of acid titrated, the normality of the reagent, and the size of the increment of reagent added in the region of the end points. In interpreting the curve obtained it is, of course, essential to take into account the value of the blank titration on the solvent.

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Determination of Carotene as a Means of Estimating the Vitamin A Value of Forage

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A SIMPLE method for routine determination of carotene in freshly cut or dried forage is presented. Its commercial uses and its value in obtaining the quantitative information essential to comprehensive work on vitamin A problems in domestic livestock are obvious.

The justification for using the carotene content of forage as a measure of its biological value with reference to vitamin A may be summarized as follows:

1. Feeding of carotene to vitamin A–deficient rats restores growth and cures ophthalmia (*2*).
2. Carotene is converted to vitamin A in the animal organism (*9*).
3. The biological values of various plant sources parallels the carotene content (*3*).
4. Neither xanthophyll nor chlorophyll, apparently, possesses vitamin A activity when fed to rats or chickens (*7, 8*). The possibility remains, however, that xanthophyll may possess some growth-promoting activity when fed to herbivorous animals (*12*). This paper presents evidence that in the unsaponifiable fraction of forage extracts all the substances that react to form a blue color with antimony trichloride decrease as the carotene diminishes. Comparative values on the basis of carotene should therefore be reasonably accurate, even though other substances contribute to the vitamin A value.
5. Pure beta-carotene is equivalent in biological value to vitamin A (*10*). Kuhn, Brochmann, Scheunert, and Schieblich (*8*) have shown that alpha- and gamma-carotene are only one-half as efficient as beta-carotene; and this result obtained by biological tests agrees with the idea that beta-carotene ($C_{44}H_{56}$), having a symmetrical formula, may, by the addition of two molecules of water, produce two molecules of vitamin A ($C_{20}H_{30}O$), while alpha- and gamma-carotene, having asymmetrical structure, can produce only one molecule of vitamin A.
6. No preformed vitamin A has been found in any plant source.
7. Biological tests can be applied only to a limited extent, time, cost, and facilities being limiting factors. Furthermore, reproducible results are obtained only with difficulty, particularly in different laboratories. The tests may be influenced by the basal diet; by the experimental rats, both in regard to initial reserve and general health; and by methods adopted for measuring growth responses and in defining "normal" and "minimal" growth. The extent of these variations in animal tests has recently been indicated by Moore (*10*), who showed that the "minimal" daily dose of carotene for rats reported by different workers has ranged from 0.5 γ to 5.0 γ. Assuming that the carotene content of a feed is determined quantitatively, the maximum error in using the amount of carotene to express the vitamin A value would be 100 per cent in case one sample contained beta-carotene and another contained alpha- or gamma-carotene exclusively. Karrer and Schlientz (*6*) have shown that carotene preparations from grasses, spinach, and nettles may be regarded as almost pure beta-carotene. Smith and Milner (*14*), examining the leaf carotenes from a number of plant sources including alfalfa, found them all high melting and optically inactive, indicating that they are beta-carotenes. Apparently, therefore, variation in the form of carotene occurring in common forage plants is a negligible factor influencing the accuracy of expressing the vitamin A value on the basis of the carotene content.

The quantitative determinations of carotene reported in this paper were made colorimetrically with the Sprague (*15*) color standard. Two methods of extraction are compared. The first one used was the Schertz (*13*) modification of the method of Willstätter and Stoll. Not being interested in determining chlorophyll, the author omitted the step in Schertz's procedure for removing flavones, which are removed later with the saponification of the chlorophyll. It also proved possible to proceed immediately with the saponification instead of allowing the solution to stand in the cold as recommended by Schertz. This was accomplished, after adding alcoholic potash to the ether solution, by distilling off the ether, boiling the residual alcohol solution for 5 minutes on the steam bath, cooling, and reëxtracting with ether.

Thoroughness in grinding the sample with sand in a mortar appears to be the most important factor influencing quantitative results with Schertz's extraction procedure. The grinding is laborious, especially with the larger samples that must be employed when the feed is low in carotene.

The following method of extraction has consistently given reproducible results, comparable to those obtained with the acetone-ether extraction of Schertz. The samples need not be finely ground, for quantitative extraction of pigment from commercial alfalfa meals has been obtained without further grinding. The author has secured 98 to 100 per cent recovery of crystalline carotene when as much as 7 mg. was added to samples of well-bleached straw and carried through the entire process.

Method of Procedure

The samples (1 to 5 grams) are weighed out and transferred to Erlenmeyer flasks, and 20 cc. of a freshly prepared, saturated solution of potassium hydroxide in ethyl alcohol are added for each gram of sample. The flasks are fitted with reflux condensers, and the contents boiled on a steam bath or hot plate for 30 minutes. If portions of the sample collect on the sides of the flask, they may be washed down with alcohol from a wash bottle. The fats and chlorophylls are saponified, and at the same time the cells are disintegrated by the action of the hot alkali. The contents of the flask are then cooled, 50 to 100 cc. of ethyl ether are added, and after shaking for a minute or so and allowing the sediment to settle, the ether-alcohol mixture is decanted into a separatory funnel. This is repeated twice more with smaller quantities of ether; then the residue in the flask, which sometimes forms an adherent mass, is broken up by shaking with a small quantity of 95 per cent ethyl alcohol. After two or three additional extractions with ether, it usually comes off colorless and the residue is then discarded. From 200 to 250 cc. of ether are usually required for the extraction.

About 100 cc. of distilled water are next poured gently through the alcohol-ether solution in the separatory funnel. The alkaline alcohol-water solution containing most of the chlorophyllines and flavones separates, is drawn off from the bottom of the funnel, and is reëxtracted by shaking gently with ethyl ether in another separatory funnel. If an emulsion is encountered, it may be cleared by adding a little ethyl alcohol. The ether extracts are combined and washed with distilled water until free from chlorophyllines and alkali. Washing three or four times by pouring the water through the solution and down the sides of the funnel removes most of the alkali. The remainder is removed by gently shaking the ether solution with small quantities of water until the wash water no longer gives a color with phenolphthalein.

The ether solution containing carotene and xanthophyll is transferred to a flask, and the ether distilled off, using a steam or water bath. Just before evaporating to dryness the flask is removed from the heat and placed in a vacuum desiccator, where the remainder of the ether is removed under reduced pressure.

The residue containing the combined carotene and xanthophyll fractions is dissolved in 30 to 40 cc. of petroleum ether and transferred to a small separatory funnel. The xanthophyll is extracted from the petroleum ether solution first with 85 per cent and finally with 90 per cent methyl alcohol. After shaking the petroleum ether solution with approximately an equal volume of alcohol, time is allowed for the emulsion to break and the solutions to clear. The alcohol layer containing xanthophyll is then drawn off from the bottom of the separatory funnel. After five or six extractions with 85 per cent methyl alcohol have removed most of the xanthophyll, washing with 90 per cent

Table I. Carotene Content and Antimony Trichloride–Blue Values of Alfalfa Meal and Leaf Meal

Sample	Description and Treatment of Sample	Carotene Content: Alcohol-ether extraction (author's modification)	Carotene Content: Acetone-ether extraction (Schertz's procedure)	Antimony Trichloride–Blue Values (Units per Gram)[a]: Carotene fraction	Xanthophyll fraction	Total unsaponifiable fraction
		Mg./100 g.	*Mg./100 g.*			
1	Commercially dehydrated alfalfa-leaf meal	13.9	13.7	120	400	500
		..	13.5	140	..	...
		13.7	13.9	140	400	500
1-a	Sample 1 after 4 hours' ultraviolet irradiation	..	10.9	100	320	...
		..	11.0	120	320	400
1-b	Sample 1 after 8 hours' exposure to sunlight	..	6.8	62	190	250
		..	6.6	62	190	250
1-c	Sample 1 after 16 hours' exposure to sunlight	..	4.2	36	60	100
		..	3.9	36	60	...
1-d	Sample 1 after 40 hours' exposure to sunlight	2.4	2.3	20	40	60
		2.3	2.2	20	40	70
1-e	Sample 1 after 5 months' storage	9.9	9.9	...	..	...
		9.8	9.9	...	..	...
2	Field-cured alfalfa hay, University Farm	..	3.7	45	160	120
		..	3.8	40	..	100
2-a	Sample 2 after 5 months' storage	3.4	3.2	...	..	...
		3.4	3.3	...	..	...
3	Commercially dehydrated alfalfa meal	12.2	11.7	100	..	...
		12.1	11.4	...	..	...
		..	12.1	...	..	...
		..	11.6	...	..	...
4	Field-cured alfalfa meal from same cutting as sample 3	10.6	10.9	100	..	...
		10.7	10.5	100	..	...
		10.7	10.6	...	..	...
		..	10.3	...	..	...
5	Fresh alfalfa leaves, analyzed immediately (dry basis)	..	52.1	...	..	...
		..	51.8	...	..	...
6	Alfalfa leaves, vacuum-dried 3 hours at 100° C.	52.4	52.4	500	1300	...
		51.8	51.8	...	..	...

[a] A blue color unit is defined as the amount of chromogen in 0.05 to 0.2 cc. of chloroform solution that will give the faintest detectable blue color with 2 cc. of antimony trichloride reagent (saturated solution in c. p. chloroform). One color unit in terms of carotene is equivalent to 1.0 to 1.5 γ of carotene (S. M. A. carotene, m. p. 166° to 168° C.).

methyl alcohol is continued until it comes out colorless. The petroleum ether solution, containing the carotene, is washed twice with distilled water to remove the alcohol and is then filtered into a volumetric flask (usually 50 cc.) through filter paper upon which is placed a small quantity of anhydrous sodium sulfate. Filtering removes the water and clears the solution. After making the carotene solution up to volume, it is compared in a colorimeter against the dye standard. Fresh green plant tissue may be extracted as outlined above by first cutting the sample fine, then grinding with sand in a mortar, the whole being moistened with a saturated solution of potassium hydroxide in ethyl alcohol.

Preparation of the Dye Standard. The stock solution is prepared according to the directions given by Sprague (*15*), except that the dyes are made up in a single solution rather than two separate solutions. The stock solution is made as follows:

Naphthol yellow (3.06 grams) and Orange G crystals (0.45 gram) are dissolved in distilled water and made up to 1 liter. The dissolving of the Naphthol yellow is facilitated by first adding water to form a thick paste, then grinding it in an agate mortar. The standard is prepared by diluting 5 cc. of the stock solution to 1 liter. The author's dye solution, standardized against International Standard carotene, is equivalent to 2.7 mg. of carotene per liter. On the basis of S. M. A. carotene (m. p. 166° to 168° C.), the value of the dye standard is 2.63 mg. of carotene per liter.

The author's results are reported upon the basis of International Standard carotene. Different batches of dyes vary and must always be standardized against carotene. The stock solution is quite stable, and the standard solution changes very little over a period of 2 months when kept in the dark.

$$\frac{\text{Depth of standard}}{\text{Colorimeter reading}} \times \frac{100}{\text{amount of sample in grams}} \times \frac{\text{total volume of unknown}}{1000} \times \text{value of standard in mg. of carotene per liter} = \text{mg. of carotene per 100 grams of sample.}$$

The results obtained with the alcohol-ether extraction method are compared in Table I with those obtained with Schertz's procedure. Individual determinations on the different samples are included to show the degree of variability. The carotene determinations have been supplemented in some cases by antimony trichloride–blue values on the total unsaponifiable matter of extracts of alfalfa-meal and leaf-meal samples, and upon the carotene and xanthophyll fractions thereof, using a dilution technic. Variation in the antimony trichloride–blue values may be expected because of the difficulty of judging the end point. The antimony trichloride–blue value for carotene, however, gives results that agree remarkably well with the colorimetric carotene determinations; it approximates a value of one blue unit for each gamma of carotene.

As the carotene content decreased under the conditions to which sample 1 was subjected, the antimony trichloride test showed a corresponding decrease in the xanthophyll and in the total chromogenic substances in the unsaponifiable fraction. Though this decrease was not in all cases proportional to that of the carotene, the trend was sufficiently close to show that no serious error would be involved in comparing the biological value of different feeds on the basis of carotene, even though xanthophyll or other substances contributed to the vitamin A activity.

Description of Samples

A brief description of the samples represented in Table I is included because the results themselves may be of some general interest.

Sample 1. Sample 1, on which animal tests were conducted, may serve to some degree as a reference for applying carotene determinations to practical feeding of poultry. This was the commercially dehydrated alfalfa-leaf meal used in A-avitaminosis experiments with chickens and turkeys (*5*). Eight per cent of this meal in an otherwise vitamin A–deficient diet permitted normal growth and prevented symptoms of vitamin A deficiency in turkeys. Four per cent in the same ration fed to chickens produced similar results. The birds were fed from hatching to 30 weeks of age. In both cases, however, the liver storage was markedly less than in birds more abundantly supplied with carotene-rich foods (yellow corn and access to fresh greens). The experiments with chickens and turkeys were run several months before the carotene determinations were made, so that the leaf meal had time to deteriorate somewhat. During a subsequent 5 months' period, while stored in a covered can at room temperature, the meal lost about 28 per cent of its carotene, as shown by sample 1-e. The material was very finely ground. Possibly, the loss may be slow at first and become accelerated with time. Data presented by Frapps and Treichler (*4*) indicate this to be the case, although contrary results are indicated by Russell,

Taylor, and Chichester (*11*). The factor of environmental temperature during storage should be considered in this connection.

A biological test with rats was conducted by Caldwell and Johnson (*1*) in this laboratory. Twelve rats, each fed 60 mg. of the leaf meal per week, made an average weekly gain of 5.7 grams, indicating a value of considerably more than 100 Sherman units per gram.

Small portions of this dehydrated leaf meal were treated in various ways. The decrease in carotene resulting from irradiation by a quartz mercury lamp (sample 1-a) was probably caused more by the oxidizing activity of the ozone than by the irradiation. The samples exposed to sunlight (1-b, 1-c, and 1-d) were spread out in a thin layer in trays covered with window glass; they were then placed on a roof where they received sunlight (October) from 8:00 A. M. to 5:00 P. M., and were stirred twice daily. Bleaching occurred, so that the samples could be readily placed in order of time of exposure on the basis of the green color. The degree of greenness has, however, serious limitations in indicating the relative carotene content of different samples, especially when leaf meals are compared with meal made from whole plants.

SAMPLE 2. Sample 2 was fine-stemmed, fairly leafy alfalfa hay cured under average conditions of exposure involving considerable bleaching. It was chopped and stored in a dark loft. Sample 2-a was taken after 5 months of storage.

SAMPLES 3 AND 4. Alfalfa-meal samples 3 and 4 were prepared by a commercial concern, whose records show that the hay was cut after 24 days' growth, from adjoining checks in the center of a field. The hay for both lots was cut at the same time (7:30 to 8:00 A. M.). The lot to be dehydrated was immediately raked into windrows and loaded on trucks. It was dehydrated at 9:00 A. M. and milled and sacked at 10:00 A. M. The field-cured lot was raked into windrows at 9:00 A. M. and cocked at 11:00 A. M.; the cocks were turned at 8:00 the following morning. At 4:00 P. M. it was loaded on trucks to be hauled to the mill, where it was ground and sacked at 9:00 the second morning. Thus the field-cured hay was exposed to sun in the swath only 1 hour and in the windrow and cocks about 24 hours. High summer temperature and dry air found in the interior valleys of California make possible such rapid curing. Samples of these lots were graded in Washington by officials in the Bureau of Agricultural Economics as follows:

Sample 3. U. S. No. 1 extra green, fine alfalfa meal, green color 83 per cent.

Sample 4. U. S. No. 1 fine alfalfa meal, green color 74 per cent.

The carotene determinations show the rapid decrease under exposure to sunlight and air, and the great variability in carotene content of hay that may occur under different conditions of curing. Comparison of samples 3 and 4 shows that under favorable conditions a field-cured product may closely approach dehydrated meal in vitamin A value. Little or no loss, apparently, occurs in vacuum drying for 3 hours at 100° C. The high value of fresh or vacuum-dried leaves compared with commercially dehydrated leaf meal indicates that relatively large losses occur in this process. The highest carotene content thus far found in dehydrated alfalfa-leaf meal was 25.3 mg. per 100 grams of sample.

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Determination of Carbonyl Compounds by Means of 2,4-Dinitrophenylhydrazine

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IN A COMPARATIVE study of methods for the estimation of carbonyl compounds, Feinberg (*4*) contrasted the completeness of reaction between certain aldehydes and bisulfite, their reaction with neutral sulfite, and the precipitation as hydrazones produced by *p*-bromophenylhydrazine and *p*-nitrophenylhydrazine.

Since that time the more highly substituted derivative, 2,4-dinitrophenylhydrazine, has been employed as a qualitative reagent by Brady (*2*) and Allen (*1*). From a quantitative standpoint this reagent would be expected to produce hydrazones of very low solubility, so that it has recently been used by Simon (*9*) and Reynolds, Osborn, and Werkman (*7*) in estimating furfural obtained from pentosans; by Fernandez, Socias, and Torres (*5*) in determining camphor, menthone, pulegone, and citral; by Clift and Cook (*3*) for certain ketonic acids; and by Houghton (*6*) for the estimation of benzaldehyde.

In the present work, the usefulness of 2,4-dinitrophenylhydrazine as a quantitative reagent has been extended to the determination of a series of representative and common aldehydes and ketones.

EXPERIMENTAL

The experimental work may be divided into two parts; first, a study of the conditions affecting the precipitation of the hydrazone, and secondly, the development of a general method based upon these findings which was applied to a series of aldehydes and ketones, both aliphatic and aromatic.

The general procedure followed in studying the various factors affecting the reaction was as follows:

A definite weighed sample of purified and redistilled benzaldehyde was dissolved in water and an aliquot sample taken which would contain approximately 37.0×10^{-5} moles. This sample was added to the freshly prepared precipitating agents which contained a definite amount of saturated 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid, varying one at a time, the time for complete reaction, the temperature, the quantity of precipitating agent, and the extent of dilution. The hydrazone was then filtered into Gooch crucibles, washed with 2 *N* hydrochloric

acid and then with water, and dried in a partial vacuum (about 90 mm.) at room temperature over sulfuric acid.

In Table I, the first series indicates the quantity of hydrazone formed from the known sample with three different amounts of the precipitant 2,4-dinitrophenylhydrazine, varying from slightly greater than an equivalent amount to an approximately 200 mole per cent excess. In each group the reaction mixture was allowed to stand at constant temperature for varying lengths of time—1, 24, 60, and 96 hours. In these runs as the length of reaction time increased the recoveries of hydrazone progressively decreased from 99.15 down to 93 per cent of the theoretical. These results indicate that the hydrazone may undergo hydrolysis in the acidic medium and the resulting carbonyl compound may then become oxidized or escape if volatile in character. At the same time the increase in the quantity of precipitant improved the total recovery of carbonyl compound as its hydrazone from 97 per cent to a practically theoretical value of 99.15 per cent. In the second series similar runs were made, employing temperatures of 0°, 50°, and 60° C. and allowing the reaction to proceed for one hour. The results in these cases definitely favor the low temperature. Finally, as shown in the third group, a markedly increased dilution of the reaction mixture after precipitation had no appreciable effect on the recovery of hydrazone. Since this is the case, it is possible to employ samples of varying concentrations, a practice which is often necessary because of the solubility variation among organic carbonyl compounds.

Table I. Results of Change of Conditions in the Determination of Benzaldehyde

Volume of 2,4-Dinitrophenyl hydrazine[a]	Volume of Aldehyde[b]	Total Volume	Temperature	Time	Weight of Precipitate	Precipitation
Cc.	*Cc.*	*Cc.*	*°C.*	*Hours*	*Gram*	*%*
			EFFECT OF TIME AND CONCENTRATION			
20	13.6	33.6	0	1	0.1031	97.17
25	13.6	38.6	0	1	0.1046	98.58
50	13.6	63.6	0	1	0.1052	99.15
20	13.6	33.6	Room temp.	24	0.1011	95.29
25	13.6	38.6	Room temp.	24	0.0988	93.12
50	13.6	63.6	Room temp.	24	0.1010	95.19
20	13.6	33.6	Room temp.	60	0.1001	94.34
25	13.6	38.6	Room temp.	60	0.0974	91.80
50	13.6	63.6	Room temp.	60	0.1001	94.34
20	13.6	33.6	Room temp.	96	0.0994	93.69
25	13.6	38.6	Room temp.	96	0.0993	93.59
50	13.6	63.6	Room temp.	96	0.0992	93.50
			EFFECT OF TEMPERATURE			
20	13.6	33.6	0	1	0.1035	97.55
20	13.6	33.6	50	1	0.0995	93.78
20	13.6	33.6	60	1	0.0976	91.99
25	13.6	38.6	0	1	0.1046	98.59
25	13.6	38.6	50	1	0.0990	93.31
25	13.6	38.6	60	1	0.0977	92.08
50	13.6	63.6	0	1	0.1053	99.25
50	13.6	63.6	50	1	0.0991	93.40
50	13.6	63.6	60	1	0.0978	92.18
			EFFECT OF DILUTION			
		Diluted to Give				
50	13.2[c]	68.2	0	1	0.0841	99.64
50	13.2[c]	73.2	0	1	0.0838	99.29
50	13.2[c]	78.2	0	1	0.0835	98.93
50	13.2[c]	83.2	0	1	0.0834	98.82
50	13.2[c]	88.2	0	1	0.0836	99.05
50	13.2[c]	93.2	0	1	0.0836	99.05
50	13.2[c]	98.2	0	1	0.0839	99.41
50	13.2[c]	103.2	0	1	0.0835	98.93

[a] 4.2 mg. per cc.
[b] 37.11×10^{-5} moles per sample.
[c] 29.51×10^{-5} moles per sample.

Method of Analysis

The optimum conditions, as determined in the foregoing experiments on benzaldehyde, were incorporated in a general procedure for the determination of carbonyl compounds by precipitation as the 2,4-dinitrophenylhydrazones. A measured sample of the aqueous solution containing a weighed quantity of the carbonyl compound was added dropwise to the saturated 2 *N* hydrochloric acid solution of 2,4-dinitrophenylhydrazine which was varied in quantity from 20 to 60 cc. The reaction mixture was allowed to stand for one hour in an ice bath. At the end of this time a definite precipitate had formed and could be filtered, then washed with 2 *N* hydrochloric acid and water, and finally dried over sulfuric acid in a partial vacuum. This procedure was used to study the precipitation of the hydrazones of acetaldehyde, acetone, methyl ethyl ketone, methyl *n*-propyl ketone, benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde, and vanillin. The results are given in Table II.

Table II. Determination of Hydrazones

	Volume of Hydrazine[a]	Volume of Aldehyde		Weight of Hydrazone	Precipitation
	Cc.	*Cc.*		*Gram*	*%*
Acetaldehyde, b. p. 20–22° C. (Eastman)	50	25	38.76×10^{-5} mole/sample	0.0823	94.82
	50	25		0.0816	94.01
	50	25		0.0815	93.90
	50	25		0.0814	93.78
	50	15	51.15×10^{-5} mole/sample	0.1102	96.16
	50	15		0.1101	96.08
	50	15		0.1099	95.90
	50	15		0.1096	95.64
	50	15		0.1091	95.09
				Av.	95.04
Acetone, purified by NaI method of Shipsey and Werner (*8*)	50	11	38.41×10^{-5} mole/sample	0.0894	97.82
	50	11		0.0886	96.94
	50	11		0.0895	97.93
	50	11		0.0884	96.72
	50	11		0.0891	97.49
	50	11		0.0896	98.04
				Av.	97.49
Methyl ethyl ketone, b. p. 79–80° C. (Eastman)	40	10	36.56×10^{-5} mole/sample	0.0907	98.48
	50	10		0.0902	97.94
	60	10		0.0895	97.18
				Av.	97.87
Methyl *n*-propyl ketone, b. p. 100–101° C. (Eastman)	50	15	35.81×10^{-5} mole/sample	0.0934	98.01
	50	15		0.0935	98.11
	50	15		0.0932	97.80
	50	15		0.0938	98.43
	50	15		0.0939	98.53
	50	15		0.0931	97.69
	50	15		0.0934	98.01
	50	15		0.0951	99.79
				Av.	98.29
p-Hydroxybenzaldehyde, m. p. 116–117° C. (Eastman)	20	18.6	37.14×10^{-5} mole/sample	0.1108	98.75
	25	18.6		0.1114	99.29
	30	18.6		0.1114	99.29
	35	18.6		0.1113	99.20
	40	18.6		9.1119	99.73
	50	18.6		0.1119	99.73
	60	18.6		0.1119	99.73
				Av.	99.39
Salicylaldehyde, b. p. 73–74° C. at 10 mm. (Eastman)	20	15.3	37.22×10^{-5} mole/sample	0.1095	97.42
	25	15.3		0.1105	98.31
	30	15.3		0.1103	98.13
	35	15.3		0.1105	98.31
	40	15.3		0.1117	99.38
	50	15.3		0.1121	99.73
	60	15.3		0.1119	99.56
				Av.	98.69
Anisaldehyde, b. p. 130–131° C. at 15 mm. (Eastman)	20	14.6	37.05×10^{-5} mole/sample	0.1161	99.15
	25	14.6		0.1166	99.57
	30	14.6		0.1171	100.00
	35	14.6		0.1180	100.77
	40	14.6		0.1177	100.51
	50	14.6		0.1177	100.51
	60	14.6		0.1183	101.02
				Av.	100.22
Vanillin (Kahlbaum)	35	9.8	37.02×10^{-5} mole/sample	0.1255	102.12
	40	9.8		0.1266	103.01
	50	9.8		0.1268	103.17
	60	9.8		0.1271	103.42
	35	13.5	36.67×10^{-5} mole/sample	0.1257	102.28
	40	13.5		0.1233	100.33
	50	13.5		0.1244	101.22
	60	13.5		0.1252	101.87
				Av.	102.18

[a] 4.2 mg. per cc.

The data for the aliphatic compounds indicate that the recovery of aldehyde or ketone as the hydrazone varied from 95.04 to 98.29 per cent, increasing as the molecular weight of the compounds became higher. The efficiency of the method was very satisfactory with aromatic compounds except in the case of vanillin which gave high results apparently due to occlusion. This error could not be lessened by repeated washings and care in precipitation. In comparison

with the two substituted hydrazines studied by Feinberg, *p*-nitrophenylhydrazine and *p*-bromophenylhydrazine on the same aromatic aldehydes, the 2,4-dinitrophenylhydrazine produces the hydrazone in quantities more uniformly approaching the theoretical values, as shown in Table III.

Table III. Determination of Hydrazones

	p-Nitrophenylhydrazine	*p*-Bromophenylhydrazine	2,4-Dinitrophenylhydrazine
	%	%	%
Benzaldehyde	98.7	92.6	99.2
Salicylaldehyde	95.3	93.5	98.7
p-Hydroxybenzaldehyde	99.7	99.9	99.4
Anisaldehyde	100.5	99.2	100.2
Vanillin	99.9	99.0	102.2

Conclusions

A study has been made to determine the optimum conditions for the quantitative estimation of carbonyl compounds as their 2,4-dinitrophenylhydrazones. In the experimental determinations, a dilute aqueous solution of the carbonyl compound was added to an excess of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid, and the reaction mixture was allowed to stand at a temperature of 0° C. for one hour. The precipitate was filtered, washed with 2 *N* hydrochloric acid and water, and dried in a vacuum at room temperature.

Determinations of the amounts of hydrazone produced from samples of nine aldehydes and ketones were made and compared with the known theoretical values with variations of −4.96 per cent for acetaldehyde, −2.51 per cent for acetone, −2.13 per cent for methyl ethyl ketone, −1.71 per cent for methyl *n*-propyl ketone, −0.85 per cent for benzaldehyde, −0.61 per cent for *p*-hydroxybenzaldehyde, −1.3 per cent for salicylaldehyde, +0.2 per cent for anisaldehyde, and +2.18 per cent for vanillin.

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Determination of Small Quantities of Antimony in White Metals

A Volumetric Method

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A METHOD for determining antimony accurately has been developed in this laboratory as applied to solder, pig tin, and lead analyses, in which the antimony content is usually below 0.10 per cent. Tin and lead of high purity are used in the manufacture of solder for can-making purposes; the antimony content is uniformly low, about 0.05 to 0.08 per cent. It was on account of the tendency toward low and erratic results obtained by the available methods that the present investigation was undertaken. Valuable suggestions were obtained from a paper by Rowell (*2*).

The method as applied in the routine of white metal analysis is as follows:

Weigh a 1.5-gram sample of filings, which has passed through a 30-mesh sieve, into a 300-cc. tall-form beaker. Add 15 cc. of concentrated hydrochloric acid and 5 cc. of a saturated solution of pure bromine in concentrated hydrochloric acid (prepared by vigorously shaking 12 cc. of pure bromine with 100 cc. of hydrochloric acid in a glass-stoppered bottle). All tin-lead solders dissolve readily in this mixture. Tin will dissolve in hydrochloric acid alone, but the bromine solution should be added to insure complete oxidation. Add more bromine solution from time to time as indicated by the disappearance of the yellow color of free bromine. When solution of the sample is complete, there should be a slight excess of free bromine. Evaporate the solution to a volume of 10 cc. or a little less, and add 0.5 gram of anhydrous sodium sulfite, followed by 10 cc. more of concentrated hydrochloric acid. Evaporate again to a volume a little less than 10 cc., completely dispelling any arsenic present. Now add 20 cc. of concentrated hydrochloric acid and 40 cc. of water and boil for 1 minute while a current of air is passed through the solution. Before the final step of titration, add 60 cc. of water and titrate at a temperature of not less than 60° C., as described below.

Care should be exercised when boiling the solution to expel the last traces of sulfur dioxide. As a precautionary measure, to minimize the loss of antimony, it is best to cover the beaker with a fairly well fitting cover glass during the brief interval of boiling and agitation with the air current. The boiling need not be continued for more than a minute. Good results have been obtained by boiling for only 0.5 or 0.75 minute.

For standardizing 0.0125 *N* potassium bromate solution, the following procedure was developed:

Table I. Results of Experimental Analyses

	Sample	Weight of Sample	Antimony Added	Antimony Originally Present	Total Antimony Present	0.0125 *N* $KBrO_3$ Used in Titration	Antimony Found
		Grams	*Mg.*	*Mg.*	*g.*	*Cc.*	*Mg.*
1	Tin, Bureau of Standards, No. 42b	1.0	0.80	0.20	1.00	1.44	1.096
2	Tin, Bureau of Standards, No. 42b	1.0	0.55	0.20	0.75	1.01	0.769
3	Tin, Bureau of Standards, No. 42b	1.0	1.3	0.20	1.50	1.97	1.50
4	40–60 Solder, Continental Can Company	1.5	..	..	..	0.50	0.385
5	40–60 Solder, Continental Can Company	1.0	0.55	0.26	0.81	1.01	0.78
6	50–50 Solder from another laboratory	1.0	0.80	0.24	1.04	1.34	1.02
7	Tin, Bureau of Standards, No. 42b	1.0	0.60	0.20	0.80	1.05	0.81
8	Same as in experiment 6	1.0	0.65	0.24	0.89	1.11	0.85
9	Lead, Continental Can Company	1.5	..	..	..	0.20	0.157
10	Tin, Bureau of Standards, No. 42b	1.0	0.85	0.20	1.05	1.47	1.1
11	Lead, Continental Can Company	1.0	0.95	0.10	1.05	1.32	1.0
12	Tin, Bureau of Standards, No. 42b	1.0	0.95	0.20	1.15	1.39	1.09
13	Tin, Bureau of Standards, No. 42b	1.0	0.90	0.20	1.10	1.44	1.096
14	Tin, analysis of sample 42b	1.5	..	..	..	0.412	0.313

Place an amount of c. p. antimony powder, such that 30 or 40 cc. of bromate will be required (0.02 to 0.03 gram), in a 50-cc. Erlenmeyer flask, add 4 cc. of concentrated sulfuric acid, and heat carefully over a small flame until solution is complete, removing at once to prevent oxidation. After cooling, transfer the solution to a 200-cc. Erlenmeyer flask, and add water and 20 cc. of concentrated hydrochloric acid, so that the final volume shall be 60 to 70 cc. Heat the solution to a temperature of about 70° C., add a drop of methyl orange indicator, and carry on the titration to the disappearance of the pink color. The indicator is prepared by dissolving 0.1 gram of methyl orange powder in 100 cc. of water, and filtering the solution.

From the final buret reading 0.25 cc. is deducted. This correction factor has been found to be uniformly recurrent in a number of tests performed on blanks containing the amounts of acids and water designated above. In the routine of actual white metal analysis where sulfuric acid is not present, the end-point correction is 0.15 cc. This value was evolved in the same way as above, determining the end-point correction on blank solutions containing no sulfuric acid. In the titrations to determine the value of the end-point corrections and in the titrations of white metal analyses a 10-cc. buret was used in which the smallest graduations are 0.05 cc.

The presence of copper would prevent the use of this method, but it may be used in the presence of as much as 25 to 50 per cent of iron. The only modification required would be the addition of 15 to 20 cc. of phosphoric acid, sp. gr. 1.37 (*1*); a complex ion is formed from the phosphoric acid and ferric iron, which in a concentrated hydrochloric acid solution is very stable against the reducing agent, sodium sulfite. From this stage the process can be continued as presented.

Reference Standards

It was difficult to obtain metals or solders to be used as ultimate standards of reference for the development of this method. As far as the writer was able to determine, they were not procurable from the Bureau of Standards in Washington. It was therefore decided to use as a basis for the work Bureau of Standards pure tin sample No. 42b which was submitted to this laboratory as a standard for melting point determinations with no information as to the antimony content. Upon analyzing this sample by the present method an average of three determinations gave 0.02 per cent of antimony. From another laboratory there was obtained a sample of 50-50 solder designated to contain 0.04 per cent of antimony by the permanganate method. The average of five determinations by the bromate method gave 0.024 per cent. With these two samples as standards, the attached experimental analyses were performed.

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Iodometric Determination of Phosgene

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Data are presented that indicate the nature of side reactions causing low and erratic results by the iodometric method of determining phosgene. A simple modification is suggested for iodometrically determining all the iodine present in the form of free iodine, hydrogen iodide, and iodoacetone.

Low and erratic results have led to an investigation of the iodometric or so-called acetone method of determining phosgene (*1*, *7*), which consists of absorbing the phosgene, free from acid gases, in 2 per cent sodium iodide in anhydrous acetone and titrating with aqueous 0.01 *N* thiosulfate to disappearance of the yellow color:

$$COCl_2 + 2NaI \longrightarrow CO + 2NaCl + I_2$$

Since sodium iodide is markedly hygroscopic and can become alkaline by loss of iodine on drying (*5*), potassium iodide in saturated acetone solution (about 1.9 per cent) is a better reagent.

Beside presenting the danger of hydrolyzing phosgene

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

moisture promotes the acid-catalyzed iodination of acetone (*2*) by shifting the equilibrium in favor of iodoacetone:

$$CH_3COCH_3 \rightleftarrows CH_3C(OH):CH_2$$
$$CH_3C(OH):CH_2 + I_2 \rightleftarrows CH_3CI(OH)CH_2I$$
$$CH_3CI(OH)CH_2I \rightleftarrows CH_3COCH_2I + HI$$

Although this effect cannot be avoided during titration, it should be minimized by avoiding any prior addition of water.

Reasonable precautions did not prevent the appearance of acid in the solution. Typical results are given in Table I.

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The correct value, in the second column, was determined by saponification and Mohr determination of chlorine. The acid was determined, after titration of free iodine, by adding an excess of iodate and progressively titrating with more thiosulfate for 3 hours. Neglecting the acid gave a result, in the third column, 13 per cent too low on immediate titration and 11 per cent too low on delayed titration. Assuming formation by hydrolysis of phosgene gave a result, in the fourth column, 5 per cent too low for both determinations; the agreement indicated that the additional iodine liberated on standing was accompanied by disappearance of an equivalent amount of acid. Assuming acid formation by iodination gave a result, in the last column, 3 per cent too high on immediate titration and 0.5 per cent too high on delayed titration. The agreement between the last figure and the correct one is fortuitous, as there is no criterion for selecting the correct length of the pre-titration period.

Table I. Results by Different Methods

Minutes before Titration	Phosgene			
	Mohr method	Iodometric method		
		Iodine	Iodine + acid	Iodine + 2 acid
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
6	..	1714	1869	2025
66	1970	1751	1865	1979

The observed gradual replacement of acid by equivalent iodine, more clearly shown by the first three determinations of Table II, obtained by titrating 10-cc. portions of acetone-iodide solution through which phosgene-containing air had been passed, is incompatible with the theory of origination of acid by iodination, which, as illustrated by the last two determinations in the table, causes acid to increase with simultaneous consumption of two equivalents of iodine.

Table II. Effect of Time and Water

Water Added	Hours before Titration	0.01 N Thiosulfate Iodine	Acid	Total
Cc.		Cc.	Cc.	Cc.
None	0	5.50	0.52	6.02
None	1	5.85	0.28	6.13
None	2	5.97	0.19	6.16
20	0	5.48	0.61	6.09
20	1	4.44	1.12	5.56

The conclusion that the acid did not originate primarily by iodination can be reached independently. Others (*6*, *10*) have observed that iodination of anhydrous acetone can be prevented by excess iodide. The smallest possible molecular ratio of iodide to iodine in the experiments of Tables I and II was 6 and 30, respectively. Table III, confirming the finding of Professor Olsen that iodination does not occur unless this ratio is less than unity (*6*), shows that no iodination could have occurred prior to addition of water.

Table III. Effect of Excess Iodide on Iodination of Anhydrous Acetone

Ratio, KI/I_2	Hours before Titration	0.00684 N Thiosulfate Iodine	Acid	Iodine + 2 acid
		Cc.	Cc.	Cc.
Blank	...	12.21	..	12.21
0.00	1.5	5.29	2.81	10.91
0.20	1.0	6.84	2.49	11.82
0.40	1.25	7.99	1.98	11.95
0.60	1.25	9.46	1.16	11.98
0.80	1.25	10.83	0.62	12.07
0.93	17	11.54	0.19	11.92
1.86	17	12.34	0.00	12.34
9.30	1.5	12.23	0.00	12.23
23.2	1.5	12.21	0.00	12.21

Likewise, formation of acid cannot be explained by assuming hydrolysis of unreacted phosgene upon titrating with the aqueous thiosulfate solution, for small amounts of phosgene cannot exist in the presence of acetone. A fresh dilute solution of phosgene in acetone does not have the two specific characteristics of phosgene, its unmistakable odor and its ability to form diphenyl urea with aniline, showing that any phosgene that escaped reacting with iodide would react with acetone (*4*):

$$COCl_2 + CH_3C(OH):CH_2 \longrightarrow HCl + CH_3C(OCOCl):CH_2$$

This reaction accounts for the primary formation of acid. Although the amount of acid formed is small, it strongly catalyzes the iodination of acetone when water is added; hence, it may lead to an error much larger than itself. Many determinations of phosgene by the iodometric method have convinced the writer that prevention of this side reaction is practically impossible.

In harmony with this reaction, the progressive liberation of iodine in the determination of the acid indicated that the acid was not all in the form of hydrogen iodide (any hydrogen chloride would react immediately with iodide to give hydrogen iodide) but that some was present that reacted as a moderately strong acid (*3*). On titrating a solution made by adding acetone-phosgene solution to water and then excess iodide and excess iodate, 10.61 cc. of thiosulfate were required immediately and a total of 4.73 cc. during the next 3 hours. On similar treatment, an acetone solution of hydrogen chloride containing slightly more chloride, as shown by comparative Mohr determinations, required 16.36 cc. of thiosulfate on immediate titration and only 0.48 cc. during the next 3 hours. Progressive hydrolysis of the ester accounts readily for this difference.

Also in harmony with this reaction, precipitation of potassium chloride on adding acetone-phosgene solution to acetone-iodide required several days for completion (Table IV). In 10 days the equivalent of 11.03 cc. of 0.00732 *N* silver nitrate was precipitated; by direct titration an equal volume required 11.17 cc. On the other hand, precipitation by hydrogen chloride was probably complete within a few minutes: the precipitate formed by adding acetone-hydrogen chloride to acetone-iodide and letting stand overnight required 9.72 cc., whereas direct titration required 9.62 cc.; no further precipitation occurred during 10 days.

Table IV. Precipitation of Potassium Chloride from Acetone-Iodide by Acetone-Phosgene

Days	Silver Nitrate
	Cc.
1	8.87
3	9.82
6	10.55
10	11.03

The foregoing data indicate that the following changes occur when the iodometric method is used: Most of the phosgene liberates iodine. A little reacts instead with acetone, giving hydrogen chloride and isopropenyl chloroformate. The chlorine in these products is replaced by iodine, rapidly in the former and very slowly in the latter; potassium chloride is precipitated simultaneously. (An alternative reaction for the chloroformate is the formation of diisopropenyl carbonate by reacting with the enol form of acetone—a reaction typical of alcohols and chloroformates (*8*)—the by-product hydrogen chloride then precipitating potassium chloride.) The hydrogen iodide is slowly but quantitatively oxidized to iodine, apparently by atmospheric oxygen. Iodination of acetone occurs if the molecular ratio of iodide to iodine falls below unity, equilibrium soon being reached. As oxidation of hydrogen iodide proceeds, the equilibrium shifts in favor of more iodoacetone. When water is present, iodination, catalytically initiated by the acid from the action of phosgene on acetone, takes place regardless of excess iodide.

Since the net effect of oxidation of hydrogen iodide, when only free iodine and acid are determined, is a loss of iodine as iodoacetone, the method can be made quantitatively accurate only if iodoacetone is also determined. Fortunately this can be done in an exceedingly simple manner because of the general reaction between sodium thiosulfate and halogen-substituted alkyl groups to form compounds that do not react with iodine (chloroacetone, for example, reacts rapidly and quantitatively, *9*):

$$CH_3COCH_2I + Na_2S_2O_3 \longrightarrow CH_3COCH_2NaS_2O_3 + NaI$$

This reaction was confirmed quantitatively in the course of the study of the effect of excess iodide. At the end of four of the determinations given by Table III, 5.00 cc. of thiosulfate were added to each of the solutions. After standing for half an hour, they were diluted with enough water to permit the use of starch as indicator and then titrated to a distinct blue with 0.01 *N* iodine. Finally, the blue color was discharged with thiosulfate. As Table V shows, the total thiosulfate used for free iodine, acid, and iodoacetone agreed well with that required for the quantity of iodine used. The agreement was substantially better than for the values in the last column of Table III, since more thiosulfate was used to react with iodoacetone than with acid, due to loss of hydrogen iodide by oxidation.

Table V. Determination of Iodoacetone

Ratio, KI/I_2	Thiosulfate, Used for Iodine	Acid	Iodoacetone	Total
	Cc.	Cc.	Cc.	Cc.
Blank	12.21	..	..	12.21
0.20	6.84	2.49	2.81	12.14
0.40	7.99	1.98	2.15	12.12
0.60	9.46	1.16	1.55	12.17
0.80	10.83	0.62	0.77	12.22

Suggested Procedure

Although extraneous circumstances have prevented further experimental work, the evidence is sufficient to indicate that

the reaction between iodoacetone and thiosulfate can be used to raise the iodometric method to quantitative accuracy. The stoichiometric relations are fortunately such that errors due to the discussed side reactions, occurring because of presence of acetone, presence of moisture, or local deficiency of iodide, are corrected automatically. Thus, it is immaterial whether the acid is formed by hydrolysis of phosgene, by iodination of acetone, or by the action of phosgene on acetone. The following may prove helpful as a suggested procedure:

Absorb the phosgene, freed from acid gases, in a saturated acetone solution of potassium iodide containing at least several times as much iodide as iodine to be liberated. Add an excess of iodate and then a measured excess of 0.01 *N* thiosulfate. Let stand for half an hour or more. Make sure that the solution contains more water than acetone, add several drops of starch indicator, and titrate back with 0.01 *N* iodine to a distinct coloration. (Since excess iodate is present, 0.01 *N* hydrochloric acid probably could be used instead of iodine.) Finally, at once discharge the iodine color with thiosulfate. The total thiosulfate minus the equivalent of the added iodine then represents the phosgene exactly as if the side reactions did not occur.

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A Volumetric Method for Determination of Cobalt and Nickel

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The reaction between pyridine, the thiocyanate ion, and several metal ions (cobalt, copper, cadmium, manganese, nickel, and zinc) which results in the formation of complexes of the general formula $M(Py)_4(CnS)_2$ has been the basis for quantitative determinations of these ions developed by Spacu. Obviously the method is not applicable for one ion in the presence of any other. As all the methods of Spacu were gravimetric, it occurred to the authors that these reactions would also serve for indirect volumetric methods. As there is no reliable volumetric method for either cobalt or nickel, they were chosen to test the method. Since completion of the work, Spacu (*1*) has published a variation of the method in which he titrates the excess thiocyanate in the whole filtrate. This method did not give satisfactory results for the authors, as it was not possible to wash all the excess thiocyanate out without dissolving some of the complex salt. Spacu (*2*) has also published a potentiometric method for nickel for which he claims an error of less than 0.5 per cent.

Solutions

Standard Ammonium Thiocyanate. An approximately 0.1 *N* solution of ammonium thiocyanate was prepared and standardized by titrating it against a standard solution of silver nitrate. Potassium thiocyanate may be used in place of the ammonium salt, as later work has shown.

Standard Silver Nitrate. A 0.1 *N* solution of silver nitrate was prepared and standardized against c. p. sodium chloride.

Indicator Solution. This solution was prepared by dissolving 10 grams of ferric alum in a mixture of 80 cc. of water and 20 cc. of 6 *N* nitric acid.

Procedure

The sample, which should contain from 0.05 to 0.1 gram of cobalt as some cobaltous salt, is dissolved in about 150 cc. of water in a 250-cc. volumetric flask. The solution is made just acid to litmus with nitric acid, 3 cc. of pyridine are added, and an excess of standard ammonium thiocyanate is run in. Upon the addition of the thiocyanate, the cobalt is precipitated as pink $Co(Py)_4(CnS)_2$ which settles rapidly and filters very easily. The solution is diluted to the mark and mixed thoroughly. A portion of the solution is filtered through a dry filter and the first few cubic centimeters of the filtrate are discarded. An aliquot of 50 cc. of the filtrate is transferred to a beaker and diluted to 100 cc., 1 cc. of concentrated nitric acid is added, and an excess of standard nitrate is immediately run in. Five cubic centimeters of indicator are added and the titration is completed in the usual way. The error introduced by the presence of the precipitate in the solution is negligible.

The weight of cobalt may be calculated from the formula:

$$g = [(\text{cc. of } NH_4CnSXN) - 5\ (\text{cc. of } AgNO_3XN)]0.02947$$

In order to test the precision of the method, three solutions of cobalt sulfate were made and 25-cc. portions were analyzed by this volumetric method and also by the electrolytic method of Brophy. The results are given in Table I.

Table I. Determination of Cobalt

Solution I *Gram*	Solution II *Gram*	Solution III *Gram*
	volumetric method	
0.1328	0.1059	0.1596
0.1330	0.1062	0.1598
0.1326	0.1057	0.1594
0.1329	0.1056	0.1595
0.1326	0.1063	0.1593
0.1330	0.1058	0.1594
Av. 0.1328	0.1059	0.1595
	electrolytic method	
Av. 0.1329	0.1060	0.1596

The same procedure may be used for the determination of nickel. A comparison of the results of the method and the dimethylglyoxime method is seen in Table II.

Table II. Determination of Nickel

Solution I *Gram*	Solution II *Gram*
	volumetric method
0.0128	0.0505
0.0125	0.0507
0.0126	0.0510
0.0123	0.0510
0.0127	0.0503
0.0126	0.0504
Av. 0.0126	0.05065
	dimethylglyoxime method
Av. 0.0125	0.0506

Table III. Determination of Cobalt and Nickel in Same Solution

(Volumetric method)

Cobalt Present	Cobalt Found	Nickel Present	Nickel Found
Gram	*Gram*		*Gram*
0.0535	0.0532	0.0255	0.0254
	0.0536		0.0251
	0.0538		0.0258
	0.0539		0.0250
	0.0540		0.0248
	Av. 0.0537		0.0252

Cobalt and nickel may be determined in the same solution by precipitating them as the complex salts as outlined above, determining the nickel by the dimethylglyoxime method and calculating the cobalt by difference. The reliability of the method was tested by mixing standard solutions of cobalt and nickel sulfates to make two solutions, then analyzing for both by the volumetric method and determining nickel by the dimethylglyoxime method and calculating cobalt by the difference. The results are given in Table III.

An examination of the tables shows that this method gives excellent results for cobalt and nickel separately, and that results in the presence of each other compare reasonably well with accepted methods. The method is very rapid and requires no expensive apparatus, as does the method of Spacu for nickel.

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Volatilization of Iodine from Dilute Iodine–Potassium Iodide Solutions

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It is well known that iodine is volatilized by the passage of gases through its potassium iodide solution. The purpose of this study is to determine the magnitude of the loss under different conditions of temperature, concentration, and rate of air passage. This loss, if substantial, would have a marked bearing on the determination of reducing gases, such as sulfur dioxide and hydrogen sulfide, in the air of rayon spinning rooms and other work places.

Procedure

The apparatus used by the authors is a 500-cc. fritted-glass plate washing bottle of the Jena type. Suction is provided by a calibrated hand pump or motor driven suction pump and flowmeter. The air from the location to be investigated is sucked through the bubbler at the rate of 4.5 liters per minute until the color of the solution has disappeared or a certain definite color is reached (starch indicator is added at the beginning of the test).

From the amount of air drawn through the bubbler and the amount of iodine used, the concentration of sulfur dioxide or hydrogen sulfide can be calculated. Employing a dilute iodine solution, a test of this sort can be run in 3 or 4 minutes.

A standard iodine solution was prepared in 5 per cent potassium iodide. The iodine strength was determined by titrating with sodium thiosulfate solution which had been standardized against potassium dichromate solution. The strength of the iodine solution was 0.29035 gram of iodine per liter or 0.00228 N. In terms of hydrogen sulfide, 10 cc. of this solution are equivalent to 0.000389 gram of hydrogen sulfide or approximately 0.25 cc. of this gas at standard conditions.

Three gas-washing bottles were connected in series with a flowmeter and suction pump. Air was drawn from an uncontaminated atmosphere. The first bottle contained 60 cc. of 5 per cent potassium iodide, 5 cc. of 1 per cent soluble starch, and 10 cc. of the standard iodine solution; the second and third bottles, 60 cc. of 5 per cent potassium iodide solution and 5 cc. of 1 per cent soluble starch solution. Air was passed through this system at various rates for 12-minute periods. The temperature of the first bottle was varied, while the other two were maintained at 6° to 10° C. The iodine remaining in each bottle at the end of the 12-minute period was titrated with sodium thiosulfate solution. Results are given in Table I.

Tests were run to ascertain whether increasing the concentration of iodine in the first bottle affected the percentage of iodine lost. Doubling the amount of iodine while keeping the amount of potassium iodide the same caused a loss of 5 per cent at 7.6 liters per minute and 24° C., while tripling the amount of iodine caused the loss to increase to 13.5 per cent. A series of tests, run to determine whether increasing the total volume of solution in the first bubbler caused a change in the loss of iodine, showed that at 7.6 liters per minute and 24° C., the loss of iodine amounted to 10 per cent if the volume of potassium iodide solution were doubled.

Table I. Volatilization of Iodine

Rate of Air Flow	Iodine Remaining: First bottle	Second bottle	Third bottle
	%	%	%
	Temperature, 6–10° C.	Temperature, 6–10° C.	
L./min.			
7.6	100	0	0
	Temperature, 25° C.		
5.0	98.7	0	0[a]
7.6	98.5	1.5	0
	Temperature, 40–50° C.		
2.5	99.5	0.5	0
5.0	99.7	0.3	0
7.6	98.7	1.3	0

[a] In this one instance the second and third bottles were not cooled.

Conclusions

Air can be passed through dilute iodine–potassium iodide solutions at room temperature and at rates higher than those usually used (about 4.5 liters per minute) in gas or vapor-sampling procedures without loss of significant amounts of iodine. The loss can be cut to a minimum by reduction in temperature, in rate of air flow, or in concentration of iodine.

Although no appreciable loss of iodine may result, it would appear desirable to ascertain whether a reducing gas such as hydrogen sulfide or sulfur dioxide is completely removed from the air stream and caused to react quantitatively with the iodine at these high rates of sampling. An investigation covering this point is in progress in the authors' laboratories.

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Determination of Naphthalene in Poultry Lice Powders[1]

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A method is described for the determination of naphthalene in complex mixtures, involving removal of the naphthalene by steam distillation in the presence of alcohol and precipitation as naphthalene picrate. The precipitate is decomposed with standard alkali, the excess of which is determined by titration with standard acid, using phenolphthalein or bromothymol blue as indicator. Data are also presented for the solubility of naphthalene picrate in water and 0.2 per cent aqueous picric acid solutions.

Naphthalene is a common ingredient of poultry lice powder in which it may be found associated with sulfur, powdered tobacco, crude phenol or cresol, sodium fluoride, and pyrethrum, the base of such preparations being an inert mineral filler, generally talc or asbestine. Little information is available regarding the quantitative determination of naphthalene in this class of preparation. Collins (*3*) describes a method in which the naphthalene is extracted by a methylated ether fraction of boiling point 27° to 33° C. One-half the solvent is removed by distillation and the remainder by a current of air. The residual naphthalene is dried for 2 days in a desiccator containing a mixture of anhydrous calcium chloride and naphthalene. A direct extraction method of this kind is obviously unsuited for the analysis of mixtures containing other ether-soluble materials and thus becomes inapplicable to the majority of such preparations.

The majority of methods described in the literature are designed specifically for the estimation of naphthalene in coal gas and are based on conversion to the picrate, a crystalline additive compound, $C_{10}H_8C_6H_2(NO_2)_3OH$ (m. p. 149° C.). For example, Colman (*4*) passes a known volume of the gas through a measured amount of 0.05 *N* picric acid solution, removes naphthalene picrate by filtration, and titrates the residual picric acid with alkali, using lacmoid or phenolphthalein as an indicator. Allen (*1*) quotes Knublauch's method in which the precipitated picrate is filtered off, washed with 0.2 per cent aqueous picric acid, and titrated (decomposed) with 0.1 *N* alkali, using methyl orange as indicator.

Volumetric methods are much more satisfactory than direct weighing of the naphthalene picrate, as the precipitate must be dried at room temperature over naphthalene and calcium chloride, a procedure which is time-consuming and somewhat inaccurate owing to the unstable nature of this compound. In Colman's method, titration of the residual picric acid is not very satisfactory, because of the large volume of standard picric acid required, the fact that naphthalene picrate must be filtered off, and the unsatisfactory nature of the end point. Because of the slow rate of decomposition of the compound, the latter difficulty is still more pronounced in Knublauch's method, in which the naphthalene picrate is titrated directly with standard alkali.

In developing a method for the analysis of poultry lice powders the first requisite is the separation of naphthalene from the bulk of the substances with which it is associated. This is most readily accomplished by steam distillation, but difficulties are encountered due to stoppage of the condenser with solidified naphthalene. A method for obviating this difficulty by the addition of alcohol was developed, employing a modification of Knublauch's procedure for the determination of the naphthalene in the distillate.

Apparatus

The apparatus employed (Figure 1) consists of an 800-cc. Kjeldahl flask fitted with a steam inlet tube reaching to the bottom and connected by a Kjeldahl spray trap to a spiral condenser, the exit tube of which is lengthened to dip almost to the bottom of a 500-cc. Erlenmeyer flask used as a receiver. The connection to this flask is made by means of a two-hole rubber stopper, the second opening leading to a small wash bottle which serves as a trap. Steam is generated in a small copper boiler and superheated by passing through a short coil of 0.25-inch (0.6-cm.) copper tubing heated by a small flame.

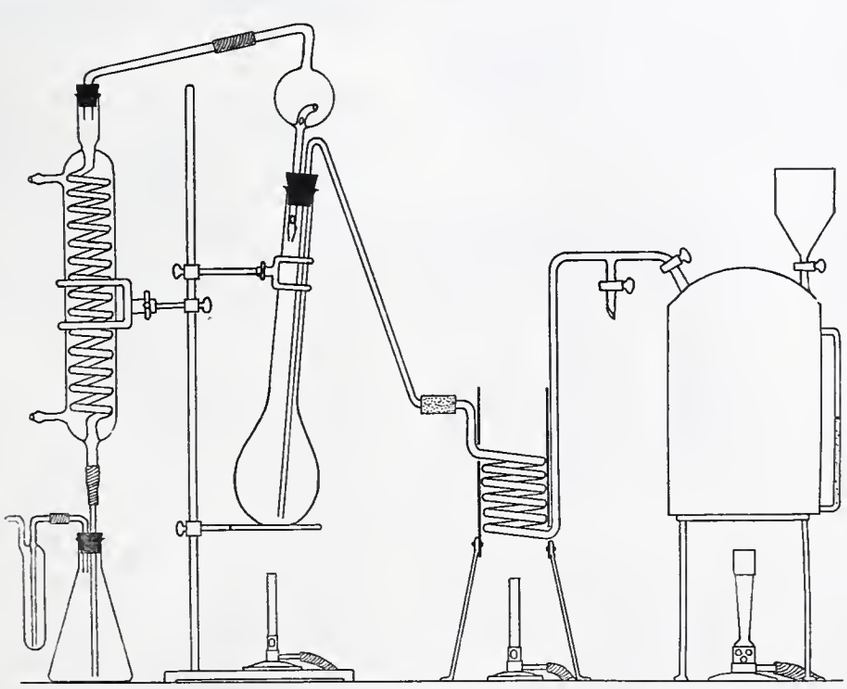

Figure 1. Diagram of Apparatus

Method

A sample weight equivalent to about 0.5 gram of naphthalene is transferred to the distillation flask, rinsing down the neck with 100 cc. of 50 per cent ethyl alcohol and 15 cc. of dilute sulfuric acid (1 to 4). Seventy-five cubic centimeters of 95 per cent ethyl alcohol are placed in the receiver and a few cubic

[1] Subsequent to the preparation of this manuscript, a paper by W. L. Miller has appeared [*J. Assoc. Official Agr. Chem.*, **17**, 308–13 (1934)] covering some of the points presented, particularly the volumetric method of determining naphthalene picrate.

centimeters in the trap. Distillation is conducted at a rapid rate until the total volume of the distillate reaches about 300 cc., the receiver having been previously marked at this volume. After distillation is complete, the condenser is removed and washed down with a few cubic centimeters of alcohol, the contents of the small trap are added to the main volume in the receiver, and any separated naphthalene is dissolved by gentle warming. Precipitation is effected by pouring the distillate rapidly and with constant stirring into 500 cc. of saturated aqueous picric acid solution contained in a 1000- to 1500-cc. beaker. The precipitate is flocculated by frequent stirring and cooled for several hours, preferably overnight, in a refrigerator. Filtration is accomplished by suction on Whatman No. 4 paper in a 4-inch (10-cm.) Büchner funnel, transfer and washing being made with the minimum amount of 0.2 per cent aqueous picric acid solution, the picrate being finally sucked as dry as possible. The paper and precipitate are then transferred to a 400-cc. beaker, any picrate adhering to the Büchner being removed with the aid of a policeman, using the minimum amount of distilled water. Twenty-five cubic centimeters of 95 per cent ethyl alcohol are then added together with a measured excess (50 cc.) of 0.1 *N* sodium hydroxide, and the beaker is covered with a watch glass and heated to boiling to decompose the picrate. After cooling, phenolphthalein is added and titration of the residual alkali made with 0.1 *N* acid.

Each cubic centimeter of 0.1 *N* sodium hydroxide neutralized by the picric acid liberated from the naphthalene picrate is equivalent to 0.0128 gram of naphthalene.

Superheated steam is not essential but greatly reduces condensation within the distillation flask and thereby tends to give more complete removal of the naphthalene, in addition to minimizing foaming, which is likely to occur in the presence of considerable organic matter.

The sulfuric acid is added to fix any nicotine that may be present, and also to insure definite acidity, as Allen (*2*) states that naphthalene cannot be quantitatively distilled from an alkaline solution.

It is essential that the picric acid used be of high purity. Heating to decompose the picrate must not be continued longer than necessary; otherwise darkening may result with consequent difficulty in determining the end point. For this reason alcohol is added to accelerate the decomposition by dissolving the liberated naphthalene. Either phenolphthalein or bromothymol blue may be used as indicator, the latter being titrated to a full yellow end point.

The results of twenty determinations with pure naphthalene are given in Table I. The material for these tests was prepared by twice resubliming Merck's C. P. naphthalene in an all-glass apparatus. The final product was fused and powdered in an agate mortar. Samples for analysis were weighed in a stoppered weighing bottle and transferred with alcohol to the distillation flask. Ten determinations were titrated using phenolphthalein and ten using bromothymol blue. Both sets of results indicate excellent recovery.

Table I. Results on Pure Naphthalene

Phenolphthalein Indicator			Bromothymol Blue Indicator		
Naphthalene taken	Naphthalene found	Recovery	Naphthalene taken	Naphthalene found	Recovery
Gram	*Gram*	%	*Gram*	*Gram*	%
0.5050	0.5008	99.1	0.5009	0.5021	100.2
0.4840	0.4866	100.5	0.4968	0.4995	100.5
0.5160	0.5124	99.3	0.5126	0.5098	99.4
0.5036	0.4995	99.1	0.4851	0.4815	99.3
0.4874	0.4853	99.6	0.5034	0.5072	100.7
0.4857	0.4853	99.9	0.4852	0.4828	99.5
0.4960	0.4995	100.7	0.4954	0.4918	99.3
0.4954	0.4918	99.2	0.5009	0.5021	100.2
0.4894	0.4879	99.6	0.4813	0.4893	101.2
0.4897	0.4893	99.9	0.5118	0.5149	100.5
	Mean	99.7		Mean	100.1

It is possible that certain other constituents of commercial lice powders may affect the recovery of the naphthalene present. In order to investigate this point, a series of synthetic mixtures was prepared closely duplicating commercial preparations. The ingredients were combined in a small porcelain pebble mill of the Abbe type, thus insuring fineness of division and uniformity of composition. The results of duplicate analyses of these mixtures, together with their composition, are presented in Table II and indicate in all cases practically 100 per cent recovery of the naphthalene present, showing that the presence of tobacco, sulfur, cresol, and sodium fluoride does not interfere with the successful application of the method.

Table II. Analysis of Synthetic Mixtures

Mixture	Composition of Mixture	Naphthalene Present	Naphthalene Found *A*	Naphthalene Found *B*	Naphthalene Found Mean
	Grams	*Grams*	*Grams*	*Grams*	*Grams*
1	Naphthalene 10.095, sulfur 20.0, tobacco 40.0, talc 130.0	5.04	5.00	4.97	4.99
2	Naphthalene 20.053, sulfur 20.0, tobacco 40.0, talc 120.0	10.02	9.99	10.02	10.01
3	Naphthalene 40.000, sulfur 20.0, tobacco 40.0, talc 100.0	20.00	20.04	20.10	20.07
4	Naphthalene 20.000, sulfur 20.0, tobacco 40.0, cresol 1.0, talc 119.0	10.00	9.91	9.99	9.95
5	Naphthalene 20.000, sulfur 20.0, sodium fluoride 50.0, talc 110.0	10.00	10.04	9.96	10.00

Solubility of Naphthalene Picrate

Obviously, the validity of the method is dependent on the removal of excess picric acid when washing the precipitated picrate, without at the same time dissolving the picrate itself. Jorissen and Rutten (*5*) state that naphthalene picrate tends to decompose on boiling a dilute aqueous solution. They give the solubility of the picrate in saturated aqueous picric acid as 3 mg. per 100 cc. of solution at 25° C. No data appear to be available regarding the relative solubility of the picrate in water and 0.2 per cent aqueous picric acid at ordinary temperatures. Solubility determinations were accordingly made using these solvents: Two wide-mouth bottles were fitted with water-sealed stirrers and sintered Pyrex glass immersion filters. Approximately 300 cc. of solvent were placed in each bottle, excess freshly prepared naphthalene picrate was added, and the whole apparatus immersed in a thermostat maintained at 25° ± 0.1° C., and stirred for 2 to 3 days. Samples for analysis were removed by suction. The content of picrate was determined by pipetting out a 100-cc. aliquot, adding a measured excess of 0.1 *N* sodium hydroxide, heating to decompose the picrate, and titrating the residual alkali with 0.1 *N* acid. Duplicate determinations were made on each solution and Bureau of Standards glassware was used throughout. The data obtained are presented in Tables III and IV.

Table III. Solubility of Naphthalene Picrate in Water at 25° C.

No.	0.1 *N* NaOH	0.1 *N* HCl	Naphthalene Picrate per 100 cc. of Solution
	Cc.	*Cc.*	*Gram*
1a	15.00	7.80	0.2574
1b	15.00	7.72	0.2600
2a	16.00	8.77	0.2582
2b	16.00	8.67	0.2617

Mean solubility of naphthalene picrate in water at 25° C. = 0.259 gram per 100 cc. of solution.

Table IV. Solubility of Naphthalene Picrate in 0.2 Per Cent Aqueous Picric Acid at 25° C.

No.	0.1 *N* NaOH	Blank Titration of 100 cc. 0.2% Picric Acid Plus 20.00 cc. 0.1 *N* NaOH	0.1 *N* HCl	0.1 *N* NaOH = Naphthalene Picrate in Solution	Naphthalene Picrate per 100 cc. of Solution
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Gram*
1a	20.00	11.52	11.31	0.21	0.0075
1b	20.00	11.52	11.20	0.32	0.0114
2a	20.00	11.52	11.26	0.26	0.0095
2b	20.00	11.52	11.31	0.21	0.0075

Mean solubility of naphthalene picrate in 0.2 per cent aqueous picric acid at 25° C. = 0.009 gram per 100 cc. of solution.

It will thus be seen that washing with 0.2 per cent aqueous picric acid solution eliminates the errors inherent in the use of water for this purpose, and if the precipitate is well sucked down and a small funnel and paper are used, no appreciable error is introduced by the adhering wash solution.

Discussion

The results obtained on a series of pure samples of naphthalene, and on synthetic mixtures containing all the commonly occurring ingredients of commercial poultry lice powders, indicate a high degree of accuracy for the suggested method. These results have been substantiated by analyses of a large number of commercial samples over a period of 3 years. The method of decomposing the picrate by an excess of sodium hydroxide and back-titrating the residual alkali has been found experimentally to offer distinct advantages over the current gas practice of titrating the residual picric acid, and is definitely superior to direct titration of the picrate itself with alkali. It is believed that this method might be advantageously adapted to the determination of naphthalene in coal gas and it should certainly prove satisfactory for the evaluation of commercial samples of naphthalene.

Acknowledgment

The authors wish to acknowledge the assistance of Louis Sair in performing a number of the analyses reported.

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Simple Apparatus for Photoelectric Titration

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PHOTOELECTRIC cells offer a means of ascertaining colorimetric end points in titration analyses which are free from subjective error. Titrations can be made by day or night, independently of lighting conditions and quite as well by a color-blind observer. Furthermore, such a method of analysis lends itself to automatic (electric) recording or control (*1*).

Because of its ruggedness and ease of operation a photovoltaic cell was chosen for the present investigation. Hitherto (*2–4*) it has been found desirable to employ some type of vernier-controlled shutter, special light filters, and storage battery, or to make use of a differential method involving an additional photoelectric cell in carrying out such titrations. In the apparatus to be described it has been found possible to dispense with all these items when using bromothymol blue as indicator. A "dead-stop" end point can be obtained accurate to better than 0.05 cc. of 0.1 *N* alkali, and greater accuracy is obtainable by plotting. This apparatus is largely, if not entirely, composed of items to be found in most laboratories, and is readily assembled.

The potentiometric set-up which is shown on the right in Figure 1 comprised a 20-inch (50-cm.) tubular, sliding rheostat, *A*, having a resistance of 390 ohms, and equipped with a rack and pinion slider which made for easy manipulation. To the slider was attached a pointer, *B*, which allowed the position of the slider to be read on a centimeter scale held in place by means of the binding posts already on *A*. A second, shorter sliding rheostat, *D*, of similar resistance gave the apparatus a wider range, as it allowed readings to be made upon a convenient portion of scale *C*. Two dry cells, *E* and *F*, furnished the potentiometer current. Two tapping keys, *G* and *H*, the former protected by the 10,000-ohm resistance *I*, were employed. The galvanometer, *J*, was of the rugged needle type, had a sensitivity of 0.3 microampere per mm., a damping resistance of 2600 ohms, and a coil resistance of 1155 ohms (*L* and *N*, type 2320-d).

Although the somewhat rough potentiometer just described has been found sufficiently accurate for the present work and those of similar construction have been used in potentiometric titration (*5*), one of the many types of commercially made potentiometers (an L and N, student type, has been found very suitable) may well prove more convenient.

The potentiometer was attached through the switch, *K*, to the photovoltaic cell, *L*, which was a Visitron, Type F2 (manufactured by the G-M Laboratories). The cell housing, *M*, consisted of a wooden box, about 21 × 7 × 7 inches (52.5 × 17.5 × 17.5 cm.), painted flat black on the inside. The end of the box, *V*, was hinged to allow light filters to be placed in slot *T* between *L* and the titration cell, *U*. This cell was simply a 2-oz. (60 cc.) bottle with fairly plane, parallel sides. A portion of the light-tight cover of *M* was removable and notched to allow for insertion of a small glass tube carrying carbon dioxide–free air for stirring. Through this notch was also inserted a small-bore glass tube which served to lengthen the buret tip so that it dipped well under the solution in cell *U* during titration. A cardboard diaphragm, *N*, with a 1.75-inch (4.2-cm.) circular opening served

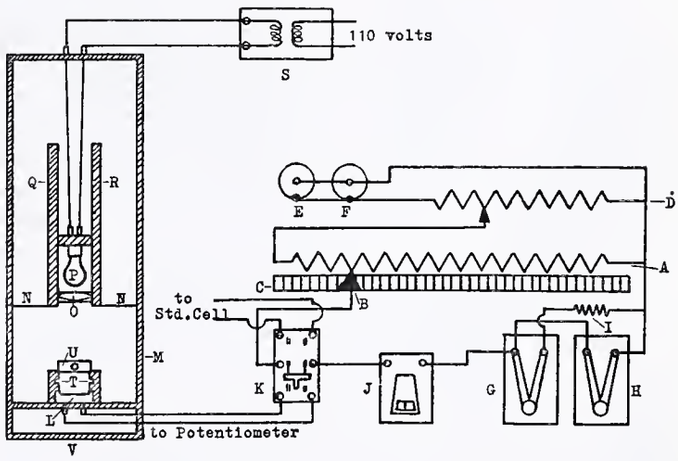

Figure 1. Photoelectric Titration Apparatus

to cut out stray light. In order to allow for focusing and variation in illumination, the small double convex lens, *O*, and the light bulb, *P*, were mounted to slide between *Q* and *R*. The light, *P*, was a 32-candlepower, 6–8 volt automobile headlight bulb which was lighted by means of current from a 6-volt transformer, *S*, which was attached directly to the 110-volt lighting circuit.

Method

The method employs the familiar Poggendorf principle of opposing the potentiometer e. m. f. to that of the photovoltaic cell and balancing by means of a galvanometer as null point instrument. The advantages of this method are well known. For the acid-alkali titrations studied, the procedure is very simple.

Having in place the titration cell containing the solution to be analyzed plus 1 cc. of 0.1 per cent bromothymol blue solution, with the air stirring and the reagent buret extension tip dipped well under the solution, the bulb is lighted. The slider is now adjusted to balance the potentiometer, and this operation is repeated after each addition from the buret. Up to the immediate

vicinity of the end point there should be no change in the e. m. f. of the photovoltaic cell, other than a slow drift or slight variation of the order of a few tenths of scale division (cm.) due to line voltage fluctuations.

This condition is illustrated by the first portions of the curves in Figure 2. At the end point the addition of 0.002 milliequivalent of sodium hydroxide will cause a wide deflection of the galvanometer needle—i. e., 10 to 15 divisions or more—which requires a 5 to 7 cm. displacement of the

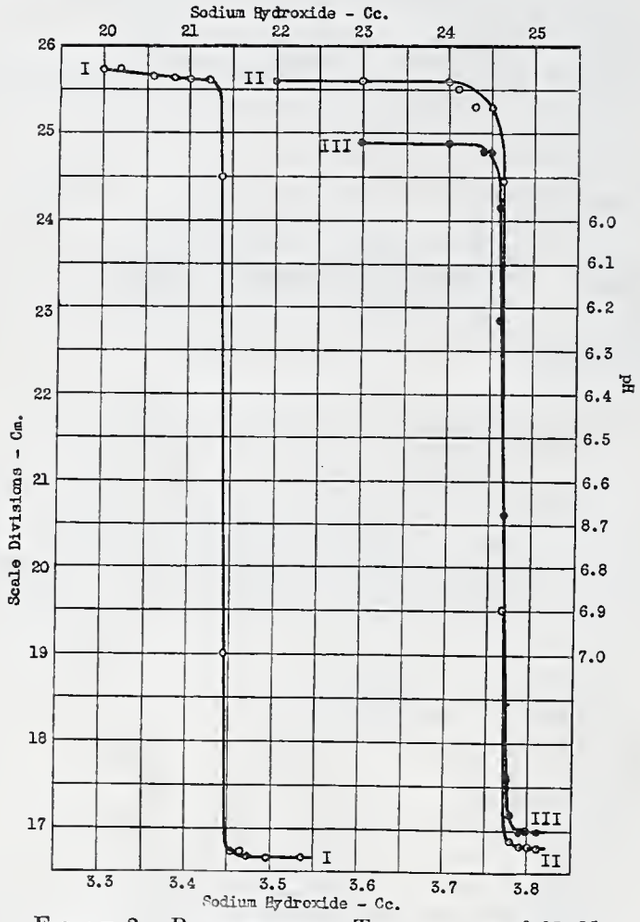

FIGURE 2. PHOTOELECTRIC TITRATION OF 0.01 *N* STRONG ACID WITH SODIUM HYDROXIDE

I. Titration of 40 cc. of 0.01 *N* hydrochloric acid with 0.1 *N* sodium hydroxide (read cc. on lower scale); II and III. Titration of 23 cc. of 0.01 *N* sulfuric acid with 0.01 *N* sodium hydroxide (read cc. on upper scale).

slider along the scale. Such a displacement is equivalent to a change of 15 to 20 millivolts—for example, a drop from around 70 to about 50 millivolts. Where a reproducibility of 0.002 milliequivalent is sufficient, the sodium hydroxide may be added in increments of this order, in the vicinity of the end point, and this single wide galvanometer deflection used as a "dead-stop" end point. Thus any scale reading or plotting of results can be avoided and titration made very rapid. When seeking agreement of 0.0005 milliequivalent or better, resort is had to recording scale readings and then to computation or plotting, as shown in Tables I and II and in Figure 2.

RESULTS

Data obtained in titrations of approximately 0.01 *N* hydrochloric and sulfuric acid, respectively, with 0.1098 *N* and 0.00926 *N* sodium hydroxide (carbonate-free) are presented in Tables I and II. In the first case a microburet was used and in the latter an ordinary high-grade buret. In these titrations bromothymol blue was employed as indicator with no light filter, and the apparatus attached directly to the 110-volt lighting circuit. The same is true of the titration graphs shown in Figure 2. The order of agreement obtainable in successive analyses is readily apparent.

TABLE I. PHOTOELECTRIC TITRATION OF 40-CC. PORTIONS OF 0.01 *N* HYDROCHLORIC ACID WITH 0.1 *N* SODIUM HYDROXIDE

No.	Readings near End Point: Buret	Scale	Change in Scale Readings per 0.01 cc. of NaOH	Computed End Point
	Cc.	*Cm.*	*Cm.*	
1	3.442	24.7	...	
	3.445	24.65	0.2	
	3.464	19.0	3.0	
	3.472	17.8	1.5	
	3.483	17.8	0.0	3.459
2	3.429	24.2	...	
	3.447	24.0	0.1	
	3.467	17.5	3.3	
	3.483	17.0	0.3	
	3.499	16.8	0.1	3.457
3	3.444	24.0	...	
	3.453	23.6	0.4	
	3.462	18.1	6.1	
	3.472	17.1	1.0	
	3.488	17.1	0.0	3.458
4	3.432	25.3	...	
	3.446	25.2	0.1	
	3.455	23.4	2.0	
	3.476	18.0	2.6	
	3.486	18.0	0.0	3.459

TABLE II. PHOTOELECTRIC TITRATION OF 23-CC. PORTIONS OF 0.01 *N* SULFURIC ACID WITH 0.01 *N* SODIUM HYDROXIDE

No.	Readings near End Point: Buret	Scale	Change in Scale Readings per 0.05 cc. of NaOH	Calculated End Point
	Cc.	*Cm.*	*Cm.*	
5	24.60	24.5	...	
	24.69	24.25	0.1	
	24.80	20.1	1.9	
	24.90	18.6	0.8	
	25.00	18.50	0.1	24.77
6	24.61	24.15	...	
	24.69	23.85	0.2	
	24.80	20.0	1.8	
	24.90	17.9	1.1	
	25.01	17.5	0.2	24.78
7	24.59	24.5	...	
	24.67	24.0	0.3	
	24.73	21.9	1.8	
	24.79	19.2	2.3	
	24.84	18.1	1.1	
	24.89	17.9	0.2	24.75
8	24.61	23.5	...	
	24.64	23.45	0.1	
	24.71	22.0	1.0	
	24.78	18.5	2.5	
	24.85	17.4	0.8	
	24.91	17.4	0.0	24.74

The accuracy of the method was examined by comparing the color of the titration solution in the vicinity of the end point with a series of bromothymol blue standards, after each addition of alkali. It is evident from the plot of pH against solution added, in Figure 2, that the end point comes too early by about 0.3 to 0.4 pH. However, because of the steepness of the titration curves this fact causes a discrepancy of only 0.05 cc. of 0.01 *N* alkali. A correction would hardly be required except for microtitration. For the determination of very small amounts of acid or where line voltage fluctuations are troublesome, the bulb filament should be lighted from a constant wattage transformer or an accumulator.

As a further application of the apparatus, iodine solution was titrated with sodium arsenite using no added indicator but employing a blue filter (Wratten No. 78). In one case 25 cc. of 0.04 *N* iodine required 4.400 cc. of roughly 0.2 *N* arsenite, while a duplicate visual titration employing starch as indicator required 4.403 cc. of the arsenite. Other applications will immediately present themselves to anyone interested in photoelectric analysis.

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Oxidation-Reduction Indicators for Use with Dichromate

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Of the various indicators suggested for use with dichromate solutions, some have proved satisfactory while others are of limited application. The present study was concerned with the discovery of still further indicators applicable to this oxidizing agent. A series of compounds of various types have been prepared or tested and the findings may be grouped as follows:

A. Compounds which give no colored oxidation products and are therefore valueless as indicators: *m*-Nitrodiphenylamine; 2,4,-dichlorodiphenylamine; 2,4,2′,4′-tetrachlorodiphenylamine; 2,4,2′,4′-tetrabromodiphenylamine; 2,4,6,2′,4′,6′-hexachlorodiphenylamine; *o*- and *m*-tolidine; tetrabromo-*m*-tolidine; diamidodiphenetole; chromotropic acid; 1-naphthylamine; *β*-*β*-dinaphthylamine; *m*-tolyl-1-naphthylamine; *o*-, *m*-, and *p*-tolyl-2-naphthylamine.

B. Compounds which give colored oxidation products but are of too little merit to warrant use as oxidation-reduction indicators: *o*-Tolylphenylamine; phenylhydrazo naphthalene; *N,N*-dimethyl-*N,N′*-diphenylbenzidine; methyldiphenylamine sodium sulfonate; ethyldiphenylamine sodium sulfonate.

C. Compounds which function satisfactorily but whose action is inhibited by mercury salts: *p*-Tolylphenylamine; *m*-tolylphenylamine.

D. Compounds which function satisfactorily even in the presence of mercury salts: Naphthidine; product derived from the action of ethyl sulfate on acetyldiphenylamine.

Indicators Found Satisfactory

Ullmann's method (*6*) is best for preparing *p*- and *m*-tolylphenylamine. Three drops of a 1 per cent solution in concentrated sulfuric acid were used in each titration. When used with ferrous solutions in the presence of 20 cc. of the usual phosphoric-sulfuric acid mixture and 15 cc. of 6 *N* hydrochloric acid, one drop of 0.1 *N* dichromate produces a deep blue coloration, easily visible in a total volume of 250 cc., and lasting for 10 to 15 minutes. The color is sharply discharged by ferrous ion and the change may be reversed as often as desired. These indicators were used in the determination of iron and chromium and the results agreed within the ordinary limits with those obtained on the same ores using ferricyanide as external indicator. The solutions are best standardized against ores of known content. For decinormal solutions the indicator error as compared with ferricyanide is 0.07 cc. for both *p*- and *m*-tolylphenylamine. However, this indicator error may be disregarded in determining the ratio between the ferrous and dichromate solutions.

Like diphenylbenzidine and its derivatives, these indicators permit of a simplification of the usual procedure employed in the determination of chromium. Instead of treating the solution of the hexavalent chromium with an excess of ferrous solution and then determining the excess with either dichromate or permanganate, the indicator may be added to the original dichromate solution and titrated directly with ferrous solution. No color appears until the addition of the ferrous solution is begun; the solution then turns deep blue and the titration is continued until the color is discharged.

Although benzidine produces an intense color in the presence of an excess of oxidizing agents, it is of no value as an oxidation-reduction indicator in strongly acid solutions (*4*). However, in the course of this study it has been found that the analogous compound naphthidine, $H_2NH_6C_{10}{\cdot}C_{10}H_6NH_2$, functions excellently under the conditions obtaining in the usual analytical procedures for iron and chromium. It gives a deep red with a slight excess of dichromate and the color is sharply discharged by ferrous ion. Three drops of a 1 per cent solution in concentrated sulfuric acid suffice for a total volume of 250 cc. Mercury salts do not interfere with the development and discharge of the color, a fact of importance if stannous chloride is used to reduce the ferric iron as a preliminary to the dichromate titration. No method for preparing naphthidine in good yield is now available; the authors' best results were obtained by reducing azoxynaphthalene with stannous chloride as recommended by Cummings and Steel (*1*).

Comparative determinations with naphthidine, ferricyanide, diphenylamine, and diphenylbenzidine as indicators proved the reliability of naphthidine, which shows a distinct advantage in that the red is in greater contrast to the green of the chromic ion than is the blue developed by the other two internal indicators. The indicator error for naphthidine as compared with ferricyanide is 0.03 to 0.04 cc. when decinormal solutions are used. The deep red oxidation product is stable for a period of 1.5 to 2 minutes after the first excess drop of oxidizing agent has been added, and then gradually fades.

Wieland (*7*), while preparing methyldiphenylamine by treating diphenylamine with methyl sulfate, obtained as a side product methyldiphenylamine sodium sulfonate. He observed that the latter gives a red color with a trace of dichromate but records no investigation of its indicator possibilities. Actual tests demonstrated that it cannot be so used, since a long range of intermediate colors precedes the development of the full red and the establishment of the exact end point is consequently obscured.

Gibson and Vining (*2*), who evidently were not cognizant of Wieland's prior study, duplicated much of his findings and also extended the study to the action of ethyl sulfate on diphenylamine. They report that no corresponding ethyl sulfonated compound is produced. Repetition of Wieland's procedure using ethyl sulfate produced this salt, which is also formed by the action of ethyl sulfate on ethyldiphenylamine by the method employed by Gibson and Vining. Analysis of the product from both these methods gave figures for sodium and sulfur which agree with those calculated for ethyldiphenylamine sodium sulfonate, $C_6H_5NC_2H_5C_6H_4SO_3Na$. The pure compound was obtained by fractional recrystallization from water. As an indicator it suffers from the same defects as the methyl compound.

Since Kolthoff and Sarver (*5*) produced an excellent indicator, diphenylaminesulfonic acid, by the action of fuming sulfuric acid on acetyldiphenylamine and in view of the fact that ethyl sulfate was found to sulfonate diphenylamine, it seemed logical to expect that a sulfonated diphenylamine would be formed by treating acetyldiphenylamine with ethyl sulfate.

Fifty grams of acetyldiphenylamine, prepared by the method of Kaufmann (*3*), and 40 grams of ethyl sulfate were heated on the water bath for 5 hours. The reaction mixture was then refluxed with a solution of 7 grams of sodium in 200 cc. of ethanol until the original dark solid had been converted into a pure white mass. The alcohol was removed by distillation and the solid residue dissolved in water. The resulting solution was thoroughly extracted with ether to remove any diphenylamine. The ether was

removed from the water layer by aëration and the solution treated with concentrated sodium hydroxide solution until a permanent turbidity appeared. A voluminous precipitate separated during the course of 12 to 24 hours and was recrystallized from water.

This material was found to function admirably as an indicator, but all attempts to isolate the pure compound proved fruitless. The analyses of the crude material indicate that it is probably the sodium salt of a monosulfonated diphenylamine and in all likelihood it is an isomer of Kolthoff's indicator. While the latter with dichromate gives a purple-red, closely resembling permanganate, the compound under discussion produces a color much less blue and more red, very similar to that of alkalinized phenolphthalein. The material after one recrystallization is sufficiently pure for use and 3 drops of a 2 per cent aqueous solution give excellent results in a total volume of 250 cc. Comparative analyses show that it is as reliable as Kolthoff's indicator for the determination of iron and chromium (other determinations have not been attempted as yet), and mercury salts are without effect on the color development. The indicator error of this compound is 0.08 cc. as compared with ferricyanide when decinormal solutions are used. The reddish purple oxidation product is stable for several hours after the first excess of dichromate has been added. This indicator is more easily prepared than Kolthoff's indicator and is obtained directly as the very soluble sodium salt, whereas Kolthoff's material is usually available only as the difficultly soluble barium salt. This study will be continued.

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Apparatus for Boiling Point and Boiling Range Measurements

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During the course of work on the fractionation of gasolines and a variety of other organic liquids it was necessary to have an apparatus that would not only give the initial boiling points of the substances (*1–3, 5–9*), but would also allow material to be distilled off and successive boiling points to be taken, thereby enabling the use of the boiling point spread as a further indication of the purity of the material. A simple apparatus similar to that developed by Cottrell (*1*) has been constructed which gives ample time for liquid and vapor to reach equilibrium without superheating, and where abundant quantities of boiling liquid and vapor are always in contact with the thermometer or thermocouple. A side tube permits any quantity of material to be distilled off, so that boiling points at any per cent distilled are easily obtained.

Apparatus

The apparatus is shown in Figure 1. Heat is supplied electrically by means of asbestos-covered chromel wire wound on the lower part of the apparatus. No. 22 wire was used because it was available, but a wire with a higher resistance would be better. Under the middle of this winding is another shorter winding of No. 28 chromel wire closely wound and covering a length of about 6 mm. (0.25 inch), connected in series with the main winding. This short winding of fine wire furnishes a hot spot which avoids the initial bumping frequently experienced when liquids are boiled. In addition the inner tube in the heated section is etched to give a rough surface. The amount of heat is controlled by an external resistance or a Variac transformer (General Radio Company, Cambridge, Mass.).

When heat is first applied, bubbles rise quickly from the short section heated by the fine wire. When the body of the liquid reaches the boiling point, a mixture of boiling liquid and vapor rises in the annular space between the two inner tubes, which are attached to each other by means of a connecting tube which allows the liquid from the very outside to circulate into the inner tube. Otherwise this section is unattached to the main apparatus, being centered by globules of glass on the lower section and held in place at the top by two or three indentations in the outer shell, a clearance of 3 mm. being allowed. The mixture of liquid and vapor which rises in the annular space between the two inner tubes impinges in a steady stream from all directions upon a copper-copel thermocouple which is used in conjunction with a Leeds & Northrup, No. 8662 portable precision potentiometer, enabling temperatures to be read to ±0.05° C. The copper-copel couple has been carefully calibrated against a Bureau of Standards calibrated couple and in addition checked against the boiling points of pure water, *n*-heptane, toluene, 2,2,4-trimethylpentane, and naphthalene. The liquid portion of the stream striking the thermocouple falls into the inner tube, where it is joined below by the condensed vapor which runs down from the condenser into the body of liquid outside the liquid-vapor annular space, and eventually enters the innermost tube. The cooler liquid in this latter tube descends to the bottom and passes out into the annular space in the heating section where the cycle is repeated. In this way free circulation is always possible.

To draw off liquid, the stopcock on the outlet tube connecting with the ring located just below the condenser is opened to give the desired rate of withdrawal. This ring is always filled with liquid running down from the condenser.

This type of apparatus, using a relatively large volume of liquid in comparison with the vapor, reduces the possibility of fractional distillation and enables reproducible results to be obtained.

To obtain boiling points or distillations at pressures higher or lower than barometric pressure, the vent at the top of the apparatus is connected to a system containing a barometer and a 40-gallon (151-liter) tank. To increase the pressure, air is added to the system, being first passed through an activated alumina drier. The vent on the liquid receiver may be connected to the system to give a pressure there equal to that in the apparatus. This is not necessary, however, when working at pressures above barometric as long as care is exercised in taking off the product, so that there is always a liquid seal above the draw-off tube in order that the pressure in the system may not be lowered by the escape of air to the lower barometric pressure. If a pressure less than barometric is desired the system including the receiver is connected to a vacuum line.

Performance

A boiling point apparatus having the dimensions shown in Figure 1 will take a charge of 40 to 50 cc. of liquid. When working with low-boiling materials such as pentane (which can be used satisfactorily if care is exercised), hexane, and heptane, a 50-cc. charge is satisfactory. On the other hand,

when materials boiling at 150° C. and above are used, the thermal expansion of the liquid necessitates a somewhat smaller charge of 40 to 45 cc. It is obvious that the larger the charge the larger the per cent that can be distilled off. With as little as 12 to 15 cc. of liquid left, both liquid and vapor still discharge over the couple; below this volume liquid contact with the couple ceases. In order to determine how little material may be used without superheating, several pure or relatively pure materials with little or no boiling point spread were distilled in the apparatus and the temperatures measured at different per cents off. The results, given in Table I, show that it is possible to boil as little as 5 to 10 cc. of liquid in the apparatus without any superheating detectable by the potentiometer used. Thus, 70 to 75 per cent of a 50-cc. charge may be distilled off before the liquid ceases to impinge on the couple or thermometer, and 80 to 90 per cent before there is any superheating. Further tests show that even though the amount of heat necessary for normal boiling is doubled, no superheating is evident under such conditions. The materials listed in Table I were all of high purity.

Table I. Distillation of Various Materials in Boiling Point Apparatus

	n-Heptane	2,2,4-Trimethylpentane	2,2,4,4-Tetramethylpentane	3-Ethylheptane	Triisobutylene
Pressure, mm.	735.5	760	760	760	737.5
Volume of charge, cc.	50	50	26	50	40
Boiling point, ° C.:					
0 per cent distilled off	97.40	99.2	122.2	142.95	176.05
10 per cent distilled off	97.40	99.2	122.2	143.05	176.7
25 per cent distilled off	97.40	99.2	122.3	143.10	176.85
50 per cent distilled off	97.40	99.2	122.3	143.10	176.90
70 per cent distilled off	97.40	99.2	122.3	143.10	176.90
75 per cent distilled off	97.40	99.2	...	143.10	176.90
85 per cent distilled off	97.40	99.2	....	....	177.0
90 per cent distilled off	97.45	99.2	...	....	....
Per cent distilled off when liquid contact with couple ceases	75	75	50	75	70
Per cent distilled off before superheating	85	90	>70	>75	75

Another boiling point apparatus was tested which differed from the one in Figure 1 in that there was no bulb on the main section above the heating element, and that the distance between the ring take-off and condenser was slightly longer, enabling an Anschutz thermometer to be used with the stem totally immersed. A 25-cc. charge sufficed for this apparatus, it being possible to reduce the liquid in the apparatus to 12 cc. and still have both liquid and vapor contact the thermometer. The volume could be reduced to 7 cc. before any detectable superheating occurred.

Table II. Comparison of Apparatus Using *n*-Heptane

	Standard Engler	Present Apparatus
Pressure, mm.	735.5	735.5
Boiling point, ° C.:		
0 per cent distilled off	95.0	97.4
10 per cent distilled off	95.5	97.4
25 per cent distilled off	96.0	97.4
50 per cent distilled off	96.0	97.4
75 per cent distilled off	96.5	97.4
90 per cent distilled off	96.5	97.4[5]

A comparison was made between the apparatus in Figure 1 and the standard Engler distillation which is widely used in the petroleum industry for boiling point and boiling range determinations. A sample of pure *n*-heptane, certified by the Bureau of Standards for knock rating purposes, was used. A 50-cc. sample was placed in the boiling point apparatus and the Engler distillation was carried out according to the regular standardized procedure for distillation of gasoline. The results, given in Table II, show that the Engler apparatus gives a boiling range even on a material which may be considered a pure substance. To make comparison easy, the Fahrenheit readings obtained on the Engler gasoline thermometer were converted to Centigrade for listing in Table II. The Engler thermometer was that used with the standard

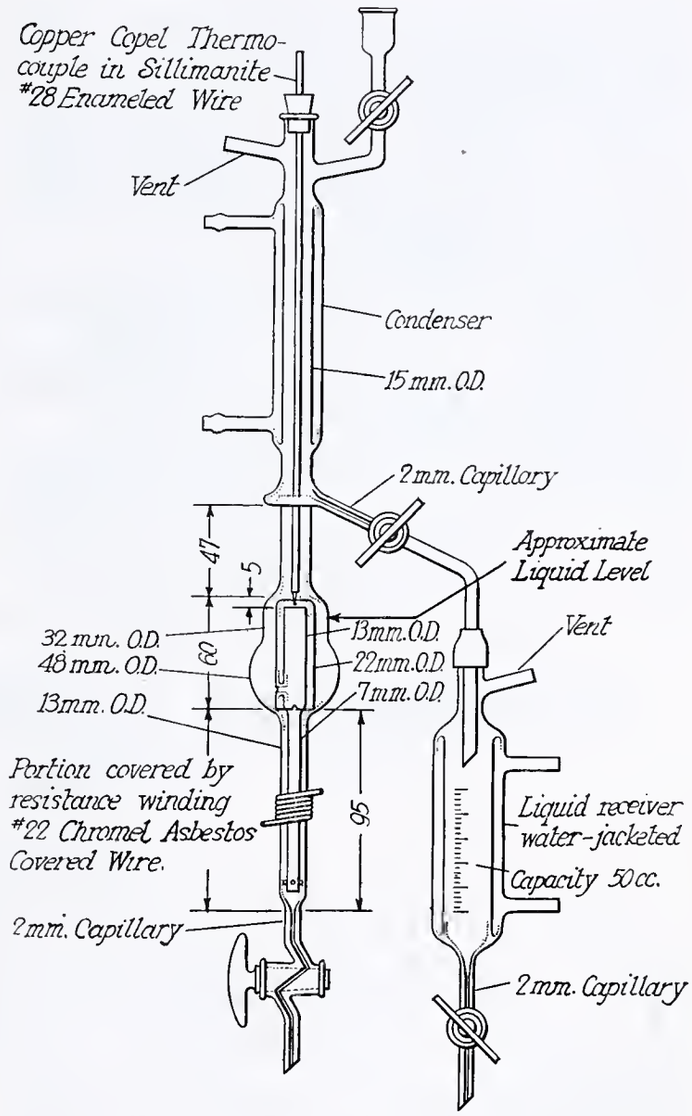

Figure 1. Boiling Point Apparatus

All dimensions in mm. Dotted lines show wall thickness.

Engler distillation apparatus and was not previously calibrated. It may be that the difference in boiling points at, say, 50 per cent distilled is due to this, but more likely it is due to the various factors regarding location of the thermometer bulb, rate of distillation, and thermometer stem corrections. The *n*-heptane when boiled at 760 mm. pressure in the boiling point apparatus checked the Bureau of Standards boiling point for this material. The data given in Table II are reproducible, having been checked at least twice.

Applications

Apparatus of this type has been used very extensively in this laboratory to determine true boiling points of a wide variety of liquids which have been subjected to fractional distillation. It not only is very useful to determine boiling points of gasoline fractions, but in addition the boiling point spread, say, between 0 and 50 per cent distilled has been used to judge the performance of fractionating columns as well as the character and purity of the materials being fractionated. When suitable corresponding fractions of the same percentage of a material which has been fractionated in the same way in different columns are tested in this apparatus, the column producing the narrowest boiling range is the most efficient.

In complicated mixtures such as gasolines, it is frequently difficult to judge inflections or plateaus in the boiling point curve of a batch fractional distillation, when temperature

is plotted against per cent distilled in the usual way. However, when the boiling point spread between, say, 0 and 50 per cent distilled is obtained in this apparatus and plotted against per cent distilled, it is much easier to detect inflections or plateaus indicating the presence of a large proportion of substances of certain boiling ranges. Again, the materials having the narrowest boiling ranges are the purest (granting no constant-boiling mixtures), for the boiling range of a pure substance with this apparatus is zero.

It is very easy and entirely feasible to use this type of boiling point apparatus to calibrate thermocouples or thermometers (*4*).

Vapor pressures can be conveniently measured with this type of apparatus by using it in conjunction with a suitable ballast tank and manometer or barometer.

Molecular weights by the method of boiling point elevation are obtained by using either one or two sets of apparatus. For this purpose the liquid withdrawal ring and side tube should be eliminated. The vapor volume compared with the liquid volume can be kept negligibly small, and the hold-up of condensed liquid is also small, so the enrichment of the liquid being boiled is slight or of negligible effect. Using two apparatus and simultaneously boiling pure solvent in one and the mixture of solvent and substance whose molecular weight is desired in the other, corrections for variation in barometric pressure are avoided.

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Apparatus for Melting Point and Micro-boiling Point

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The apparatus shown in Figures 1 and 2 has been in constant use by a large number of students for over a year and its success seems to warrant a description. To the usual conveniences attending the use of a copper block it adds the important advantages of better visibility and temperature control. The former is secured through the use of a low-power microscope and a direct light source, the latter through convenient means of heating the block or cooling it by a stream of water. An additional advantage is the possibility of determining boiling points of liquids using very small quantities of material.

As shown in Figure 1, the apparatus consists of a copper block, *A*, fixed in such a position that a removable 50-power microscope, *B*, may be focused by means of an adjustable shield on the melting point tube through the horizontal hole in the block. Illumination is provided by a 40-watt lamp, *C*, which produces no blinding effect on the eye of the observer, because of the small amount of light that enters the hole in the block and the partial blocking of the latter by the filled capillary tube. The material should not be packed solidly in the melting point capillary but lightly distributed by vibrating the tube with a file. Sufficient light is thus allowed through the substance to facilitate observation prior to melting.

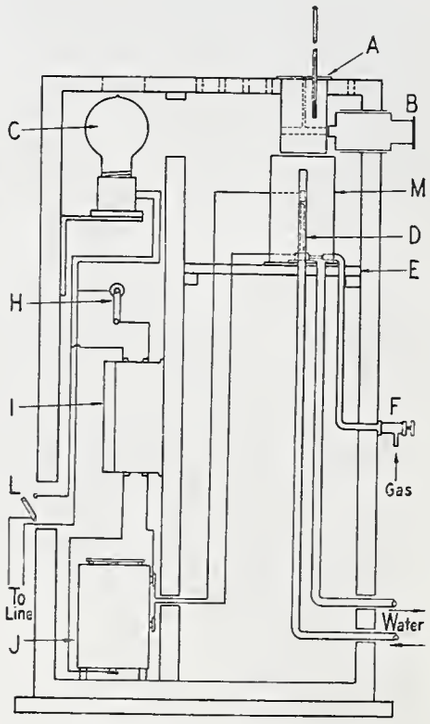

Figure 1. Side View

In the construction of the block the general directions of Friedel (*2*) may be followed, but it is recommended that a 0.125-inch hole be substituted for the prescribed slot which is difficult and time-consuming to make. This modification has been found to give excellent results.

The block is heated by the microburner, *D*, fastened to the sliding plate, *E*, and connected by rubber tubing with the needle valve, *F*. By means of the rod, *G* (Figure 2), the burner can be pushed forward under the block for heating or withdrawn for cooling, as indicated by the dotted lines. The burner is lighted by pressing the momentary contact switch, *H*, in series with the 8-volt transformer, *I*, which supplies current to the ignition coil, *J*. From this coil one wire leads to the base of the burner, the other to a copper strip, *K*, extending just over the top of the burner when rod *G* is withdrawn. The spark which results when switch *H* is pressed is sufficient to light the burner. Switch *L* controls both the lamp and the transformer.

Cooling the block is accomplished by a fine stream of water directed at its base from a brass tube enclosed by the copper cup, *M*, which is fixed in such a position on the sliding plate, *E*, that it is directly under the block when rod *G* is withdrawn. The enclosed tube is connected by rubber tubing to a supply bottle in an elevated position from which a stream of cold water can be directed on the block by turning a stopcock. A second tube in the bottom of the cup serves to carry off excess water.

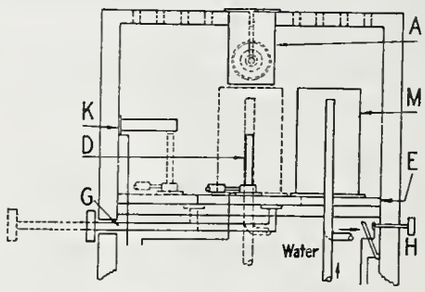

Figure 2. Rear View

The apparatus is enclosed in a wooden cabinet, shielded, for safety, in the vicinity of the block with asbestos paper. The top is made of heavy sheet iron perforated with 0.25-inch holes to allow escape of hot air and provided with a suitably sized hole in which the copper block is inserted.

Any fogging of the microscope lens due to water vapor resulting from the use of the cooling device may be easily remedied by withdrawing the microscope from its shield, drying, and replacing in position, but this procedure is unnecessary when the temperature of the block is above 100° C. The device is particularly useful in the case of high-melting compounds. The block may be heated quickly to within 10° of the melting point, the burner removed by withdrawing the rod, and a stream of water allowed to play on the bottom of the block for an instant. The rapid rise in temperature is thus brought to an abrupt halt within less than a degree. The burner may then be replaced, using a small flame so that the melting point of the compound is slowly approached. The device is also valuable in cooling the block rapidly when the melting point of a second and possibly lower-melting compound is to be determined at once. This feature is important if the apparatus is to be used by a large number of students.

Among other advantages in the use of the apparatus are: absolute safety from accidents sometimes accompanying the use of sulfuric acid baths; extreme accuracy as regards softening point, sintering, change in color or crystalline form, and melting point range of compounds; the possibility of taking higher melting points; and the use of smaller samples. This last advantage is noteworthy in the determination of boiling points by a modified Siwoloboff (*3*) method. For this purpose a large capillary tube is used as a container for a fraction of a drop of liquid and a fine capillary tube, sealed in the middle, is introduced. The former is then inserted in the block as for a melting point determination and the same procedure is followed as in the ordinary Siwoloboff method.

In Table I are given the melting points of some pure compounds observed by the use of this apparatus and by the usual sulfuric acid bath method.

Table I. Comparison of Results

Compound	Melting Point: By apparatus described	Melting Point: By usual apparatus
	° C.	° C.
Cinnamyl alcohol	27–29	27–29
p-Nitrotoluene	51–52	51.5–52
Naphthalene	79–80	79–80
Benzoquinone	111–113	111–113
Benzoic acid	120–121	120–121
Succinic acid	189–190	188.5–190
Diphenic acid	227–228	227–228
Anthraquinone	274–275	274–275
3-Aminophthalhydrazide	324–325	324–325[a]

[a] Melting point taken by means of a copper block of the Berl and Kuhlman type (*1*).

Acknowledgment

Grateful acknowledgment is made to A. A. Morton of this laboratory for his interest in the construction of this apparatus and his assistance in the preparation of this paper.

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A Converted Air-Pump Shaker

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For laboratories which are supplied with compressed air a simple shaking machine can be constructed from an air pump, a set of door springs, and a suitable frame and platform. The general principle involved is the use of compressed air to drive the shaker forward, the release of the air pressure when the piston passes some holes bored in the barrel of the pump, and the return of the piston to its initial position as the result of the tension imposed upon the springs in the forward stroke. The construction in use in this laboratory, in which an air pressure of 10 pounds is maintained at the source, is illustrated in Figure 1.

An 18 × 1.75 inch (46 × 4.5 cm.) automobile hand air pump, *P*, is altered as follows: The handle is removed, *a*, and the end of the rod is threaded and fitted with a bearing connecting to the shaking platform. The cap is removed, *b*, to reduce friction and noise. Four 0.19-inch (0.5-cm.) holes, *c*, are drilled in the barrel at 90° intervals in a line around the circumference 8.5 inches (22 cm.) from the bottom end of the pump. The size of the holes is of more importance than the position because the leather washer of the piston will catch in an opening that is too large. The air valve at the bottom is removed and the hole bored out to 0.25-inch (6.4-cm.) size, in order to admit air rapidly to the cylinder. The reconstructed pump is held in place by two large pipe clamps, *C*, which are mounted either on adjustable metal stands or wooden blocks so that the barrel is in line with the shaker platform.

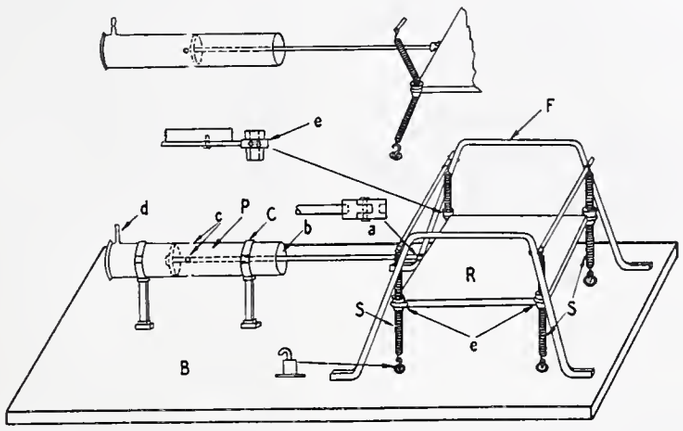

Figure 1

A set of door springs, *S*, which are 0.44 inch in diameter × 12 inches (1.1 × 31 cm.) long [their position is such as to make an 8 × 12 inch (20 × 31 cm.) rectangle] are held between the top of a frame, *F*, and the base, *B*. Only slight tension is needed. A certain amount of adjustment can be had by means of screw hooks. A machine hook with a lock washer is better than a wood screw, since the latter has a tendency to work loose.

The shaking platform is made and attached as follows: Between the front and rear pairs of springs two brass rods, threaded on each end and fitted with 0.625-inch (1.6-cm.) pipe holders, are attached. To secure a good grip a rubber stopper, bored to fit snugly, is first slipped over each spring so that the pipe clamp is pulled down upon the rubber. The author's attachment was made 3.75 inches (9.5 cm.) from the lower end of the spring. It is obvious that a longer stroke is secured if the attachment is made near the center of the spring, but because of the nature of the frame used it was impossible to make a perfect adjustment at this point. A board is next mounted on these brass cross pieces by means of U-fasteners or screws. Connection is made to the piston rod of the pump as indicated before. A box or other suitable receptacle may then be fastened on the platform. The frame is made from 0.75-inch (1.9-cm.) channel iron bent into the shape indicated in Figure 1 and made rigid by cross pieces. The whole apparatus is mounted on a wooden base, 40 × 12 × 1.75 inches (101 × 31 × 4.4 cm.)

Minor adjustments which may be made with each assembly are: moving the position of the barrel by sliding it through the pipe clamps, *C*, until proper release of the air is made at the end of the stroke, increasing the number (but not the size) of the holes where air is released, increasing the size of the air inlet, and adjusting the tension and the position of the platform. When correctly assembled and regulated, the machine should start promptly with admission of air at *d*, run continuously, and require no further adjustment for loads which vary from a gram to 1.5 kg. Higher weight limits have not been tried.

The arrangement given in this description is for an apparatus in which only a few changes have been made with the starting materials. Since the stroke in this machine need not be more than 2 inches (5 cm.) long at the most, it should be possible to cut down the length of the barrel and piston rod to proportionate size, reducing the apparatus to almost half the space formerly occupied. It should also be possible to mount the barrel under the shaking platform by use of suitable connections. The use of smaller springs will give a longer stroke. The same system of springs may be used with some advantage on motor-driven shakers.

ACKNOWLEDGMENT

The author is indebted to E. C. Curtis for valuable aid in the construction and assembling of this apparatus.

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Apparatus for Measuring Adhesion of Dried Films

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THE force of adhesion between two solids, limited in particular to the molecular attraction exerted at the interface, has been and still is subject to more empirical than exact information, particularly when the materials concerned are organic films and metal surfaces. While it has been comparatively simple to determine whether two substances adhered to each other, it has been in only rather vague terms that we could describe how well or why they adhered. Further, there has been only empirical differentiation of the two factors of molecular and mechanical adhesion.

The well-known classical researches of McBain and his coworkers gave us our first, most complete, and only systematic analysis of the fundamentals underlying adhesion. The determinations of adhesive strength were made by breaking joints by hand or by pulling apart in a tensile-strength machine. Within the limits of the determinations the data could be applied to the paint and varnish industry.

This industry has been particularly concerned with these problems as they affect both wood and metal surfaces. Not only does adhesion play an important part in the weathering and age-resistance of a film but it is of great importance where mechanical flexing or abuse is encountered. Very satisfactory advances in the practical development of adherent coatings have been made using empirical tests, such as scratching with a thumb nail, lifting with a knife, or severe bending and crimping. The authors at one time tested the adhesion of enamels to tin plate by pounding the sample with a certain hammer on a specific wooden laboratory floor. If the coating held until objections came from others in the laboratory, it was considered very adherent.

It has been desirable to set up for the coating industry a testing method which would disclose the more minute variations in adhesiveness, would give more easily reproduced results, and would allow a more fundamental study of the phenomena to be made. An ideal test method would meet the following requirements:

1. It should be easily reproducible with similar coatings under identical conditions.
2. It should be adaptable to any organic or even inorganic film.
3. Normal drying or baking of the film should be possible.
4. The film should be unchanged by subsequent treatment prior to test.
5. The test should not deform or mechanically alter the film.
6. The test should be independent of the rate of application of stress.
7. It should show adhesion at all parts of the area under test and should give a measure of the adhesion at each differential unit of the area whether of uniform adhesion or not.
8. Adhesion expressed in numerical terms should not be affected by changes in hardness, flexibility, elongation, or plasticity of the film or by the effect of internal friction as shown in the relation of slow or sudden bending or shock.

Several proposals have been made for measuring the adhesion of films to solid surfaces in mechanical units of force. Van Heuckeroth and Gardner (*9*) imbed a fabric strip in the film and measure the force required to strip the film from the underlying base. Gelva (*8*), in a method now being developed, cements a metal plug to the film after the film has dried on the base and measures the necessary rupturing force. Schmidt (*6*, *7*) glues a wood block to the film, cuts the film at the edge of the block, and, using a balance with water as the tare, obtains from a direct pull the force necessary for release in grams per square centimeter. Douglas and Pettifor (*3*) describe an "energy-absorption" test for the adhesiveness of glue to wood. A strip of strong webbing is glued to the wood panel and is then pulled off by a pendulum-type machine measuring the energy required for detachment. Christopher (*2*) describes the U. S. Bureau of Standards method for determination of the adhesiveness of bituminous coatings to steel in which a straight-pull method is used. Hart (*4*) has designed an apparatus which gives a measured impact to a coated panel and affords a comparative indication of the adhesion and brittleness. For determining the adhesive strength of surgical plaster there is a standard test in which a tensile-strength machine measures the force necessary to strip the tape loose from a plate, the force being applied to the tape in a direction parallel with the adhesive surface (*1*, *5*).

These methods, valuable as applied to specific industries and giving in general interesting comparative results, have nevertheless certain limitations. In some the drying or baking of the film cannot be carried out under normal conditions. In others, the dried film may be changed by solvent or adhesive. In attempts to apply a load normal to the surface, the angle of applied force is apt to vary. The tensile-strength-of-bond method dependent on sudden application of stress may confuse brittleness with lack of adhesion. In most

of the methods the assumption is made that adhesion is uniform over the area under test. Deformation of the film itself, which may be plastic and may require variable stresses, may give variable results. Some of these methods are not applicable to brittle films.

Proposed Method

With the hope of eliminating some of the variables and obtaining a more accurate measure of the energy involved in separation of a film from a metal, a somewhat different method is proposed, which consists essentially of stripping the metal, in the form of a thin foil, from the immobilized film. The following advantages are anticipated:

1. No variable is introduced as the nature of the film is changed from brittle to flexible, rigid to plastic, or amorphous to crystalline. For instance, as certain polymers change in properties with variation in the number of polymeric units, the change in adhesiveness may be followed without correction for changes in other properties.
2. The energy involved seems to be independent of the speed of separation.
3. Variations in adherence over the area under test are indicated.
4. A permanent record is available showing total energy required and any characteristic variations.
5. With a possible correction for the energy of deformation of the metal foil, results are independent of the angle of pull, at least within the limits imposed by the test method.

The use of metal foil in this manner allows the pull to be applied to the material having the better combination of tensile strength and elasticity with maximum flexibility. Foils of tin, aluminum, zinc, copper, silver, and lead are available and may be given any mechanical, chemical, or electrolytic pretreatment desired. The method is offered, however, principally in the hope of developing a better means of studying the fundamentals of adhesion between organic films and metal surfaces.

It is expected that complete data will later be secured, using the same mechanical arrangement and pulling the films from the rigidly held metal base, using the method of Gardner (*9*) for holding the film. Such data may show (1) that for some range of flexible films the two methods of either flexing the film or flexing the base are interchangeable, (2) that for very brittle films the films should be held rigid and the base made flexible, and (3) that for very flexible films it may be a definite advantage to work with a rigid base.

This preliminary paper deals with data on the use of a flexible base metal while the film is held rigid.

Preparation of Samples. The varnish to be tested is applied by any convenient method to one surface of a section of metal foil. In the present tests in order to avoid unnecessary variables the authors have standardized upon aluminum foil of 0.127-mm. thickness obtained from the Aluminum Company of America. This is coated in 10 × 25 cm. sections by spraying. Three coats have been used in all the following tests. After drying, the surface of the varnish film and also the surface of a 7.6 × 25 cm., 18-gage steel panel are coated with cement (sold commercially as Bakelite cement BC-6052). After drying for 24 hours the cement surfaces are pressed together and passed manually through steam-heated rollers in approximately 30 seconds to secure contact. For this purpose an ordinary clothes wringer provided with steam-heated brass rollers has been used. The temperature of the roll surfaces is approximately 170° C. After cooling it is usually found that as the test load is applied the foil can be pulled off, leaving the varnish film firmly cemented to the steel panel. For test the foil is trimmed even with the edge of the steel panel or slit with a razor blade to strips of suitable width.

Apparatus. A rigid level supporting table *A* is provided upon which the prepared specimen may be secured. In Figure 1 are shown steel panel *B*, cement layer *C*, varnish film *D*, and metal foil *E*.

The loosened end of the foil is attached by means of clamp *F* to cord *G*, the opposite end of which is attached to the movable recording spring balance, *H*. This balance carries a pen, *I*, which traces a record on chart *J* as the foil is removed. Ball bearings are used throughout and adjusted to run as freely as possible. The end of the spring on the balance is connected by a cord, *K*, to a pulley, *L*, to apply the load. This pulley is connected through a reducing gear and clutch to a motor for constant-speed drive.

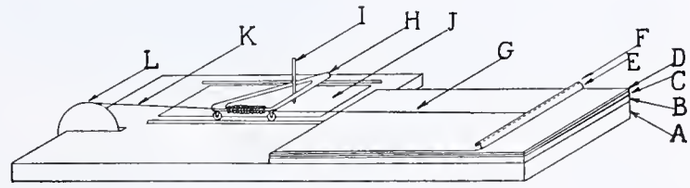

Figure 1. Diagram of Apparatus

Any sensitive tensile-strength apparatus could be adapted to this purpose, but since none delicate enough was available in the laboratory, the one described was constructed. A Scott tester, especially if provided with a recording mechanism, would be ideal.

Test Procedure. The prepared test piece is secured to the table and the end of the foil attached to the clamp. The clutch is thrown in so that the recording balance, pulling the foil after it, is drawn across the chart. The force required to rupture the bond between film and metal is then recorded as ordinate, while the abscissa shows twice the length of foil removed. Typical charts are shown in Figure 2. The spring balance was calibrated to give grams load necessary for an extension of 1 mm., the calibration being done on the apparatus itself in order to compensate for friction.

With a chart of the type shown in Figure 2, knowing the spring calibration (in this case 63.1 grams per mm.), we are able to calculate the energy, or force times distance, which is required to separate a unit area of metal-film interface. For absolute values a correction must be applied to these figures for the energy required to deform the metal foil and straighten it again. For practical laboratory varnish testing where comparative results alone are satisfactory, such a correction is not necessary.

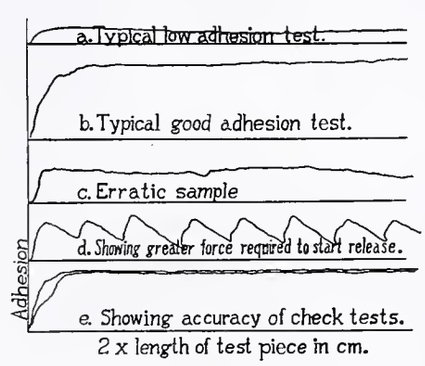

Figure 2. Typical Adhesion Charts

All adhesion figures in this paper are expressed in gram centimeters of energy per square centimeter of interface without correction for the foil, although the foil correction will be discussed below.

For most routine work the total energy could readily be determined by removing the foil with a pendulum mechanism by a method similar to that proposed by Douglas and Pettifor (*3*) for glue bonds. Such a method would not, however, give a complete record of the entire test specimen. Gardner (*9*) states that the pull is usually constant for the entire length of the test, although in two tests where adhesions of 0 are given in his tables, footnotes indicate that once the force reached 400 and 1400 grams, respectively. Uniformity undoubtedly exists in such adhesion as is obtained with lacquers to metals, and the authors have found it also with varnishes of poor adhesion. (*a*, Figure 2.) As the adhesion improves, on the other hand, differences may become more apparent (*b*, *c*, *d*, Figure 2). With varnishes of strong adhesion the value may or may not be uniform (Figure 2). It was the original intention to measure the area of these adhesion diagrams by means of a planimeter and compute the average energy. So far the authors have been unable to

explain many of the variations and have taken the maximum adhesion for their values rather than the average, being not yet sure which figure is of primary importance. Fortunately, in most cases, the curves have been fairly flat.

One interesting type of curve is shown in Figure 2, *d*. A few varnishes seem to have the property of strongly resisting the initial bond rupture, but once it is started, continue to rupture under a much lower stress, producing the jerky curve shown here. This difficulty is not often encountered but is being investigated further with hope of eliminating it.

Experimental Data

A series of seventy different varnishes have so far been tested and tentatively evaluated. It is well recognized that aging and weathering have profound influences upon the thorough drying and adhesive properties of varnish films, but thus far the authors have not had time to follow these characteristics. It is the purpose of this paper to outline a method by which adhesion may be measured, giving a few observations on its use with varnishes of varying composition. Studies are in progress to determine the effect on adhesion of variations in cooking, compounding, aging, weathering, etc.

Since their studies of these factors are so incomplete at present, the authors wish to avoid confusing discussion by giving only a few figures to show that the method can differentiate practical variations in adhesion and that it is reproducible and accurate.

For this purpose in Table I adhesion values are given for a number of varnishes, air-dried for 3 weeks. No. 9, an old-fashioned, fossil resin varnish of accepted good adhesion, is given as a sort of bench mark, while the other figures give some idea of the wide variation to be expected from synthetic resins by reason of variations in compounding and cooking.

Table I. Adhesion Values of Air-Dried Resins

[All varnishes 45 kg. of resin to 170 kg. of oil (50 gal.) using various oils and resins cooked by various methods. Varnishes dried and aged 3 weeks.]

No.	Description	Adhesion G.-cm./sq. cm.
9	Old-fashioned fossil resin varnish, congo-linseed	967
10	Commercial resin No. 7, tung oil	568
16	Commercial resin No. 8, tung oil	736
17	Commercial resin No. 9, tung oil	673
18	Commercial resin No. 10, tung oil	757
19	Commercial resin No. 11, tung oil	799

In Table II are given values for a number of varnishes which for lack of time had to be force-dried. Here as a bench mark a rosin–ester gum varnish was used, which rather surprisingly shows the same value as the congo-linseed varnish No. 9 in Table I. The other varnishes are all made with synthetic resins. These figures are given only to illustrate the way in which varnishes may be classified to show differences of adhesion under definite conditions.

Table II. Adhesion Values of Force-Dried Resins

[Varnishes 45 kg. of resin to 170 kg. of oil (50 gal.) air-dried 24 hours, force-dried 24 hours at 160° F. (71.1° C.)]

No.	Description	Adhesion G.-cm./sq. cm.
20	Rosin–ester gum, tung oil	967
21	Commercial spar No. 1	799
22	Commercial spar No. 2	841
23	Commercial resin No. 1, tung oil	715
24	Commercial resin No. 2, tung oil	757
25	Commercial resin No. 3, tung oil	1051
26	Commercial resin No. 4, tung oil	883
27	Commercial resin No. 5, tung oil	1051
70	Commercial resin No. 6, tung oil	1304

Reproducibility of results is best shown by Figure 2, *e*, which gives curves from duplicate determinations. Determinations must be conducted under controlled conditions as to temperature, humidity, time of drying, etc., to secure check results such as are indicated. Under such conditions the characteristic curves of Figure 2, *e*, give values of 2902 and 3028 gram-cm. per sq. cm. or a check within 2 per cent. This is better than the average. In much of this work at least three check tests have been made, and if the discrepancies are over 5 per cent, more tests are made until consistent results are obtained. Checks are usually well within 5 per cent, however.

The correction for energy required to deform the foil was mentioned above. Of course the energy which is being measured is the sum of that required to bend the metal foil and that required to separate the metal-varnish film interface. In order to know the absolute energy of adhesion we would have to know the value of the energy used in bending the foil, or else use a foil of zero thickness requiring no energy to bend. The latter is, of course, out of the question. The authors have made some attempt to get at this factor by determining apparent adhesion of two different varnishes over a range of foil thicknesses (Table III and Figure 3). They had hoped to be able to use still thinner foil, and although so far it has been found too fragile, are continuing refinements in the method of preparing samples.

An extrapolation of these curves (if such extrapolation is warranted) to zero thickness should give absolute adhesion, free of the factor of metal deformation. For practical paint and varnish study, however, there are several reasons for avoiding this. For greater adhesion, as in the case of varnish No. 3, the metal foil will be deformed to a greater extent than for lesser adhesion, as in the case of varnish No. 1. Consequently more energy is used in deforming the metal and the correction would have to be different for each degree of adhesion. It would be possible to determine apparent adhesion on different metal thicknesses for a wide range of adhesion and plot actual adhesional energy against apparent adhesional energy, so that reference to the curve would give the correct value. For some of the investigations to be conducted it is hoped to do this. All the discussion of this correction depends, however, either upon the assumption that the extrapolation of the curves in Figure 3 is justified, or upon ability to use thinner foils and extend the curves far enough to feel fully justified in only a slight extrapolation.

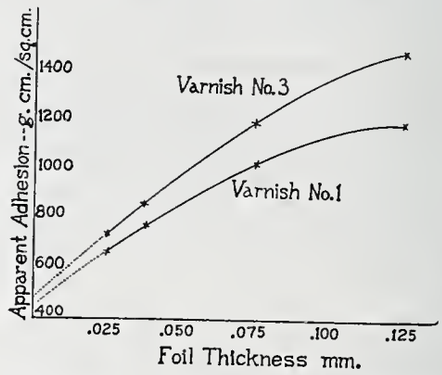

Figure 3. Apparent Adhesion of Varnishes

Table III. Adhesion over Varying Foil Thickness

Varnish No.	Foil Thickness Mm.	Adhesion G.-cm./sq. cm.
1	0.025	631
1	0.037	758
1	0.075	1006
1	0.125	1172
3	0.025	715
3	0.037	841
3	0.075	1176
3	0.125	1472

In so far as varnish testing is concerned, it is of advantage to use foil at least 0.127 mm. thick without correction. This is strong and sturdy enough to be easily handled without wrinkling or tearing, and in addition (Figure 3) its use magnifies differences in adhesion, which simplifies testing and evaluating. While the figures obtained are only relative, for varnish plant work that is all that is needed.

As for the effect of speed of separation of the interface, the authors have operated at rates between 2.5 and 3.5 cm. per second, the limits for their instrument as it stands, with check-

ing results, but in the case of most very green films the varnish next to the interface remains tacky, or in the nature of a viscous liquid. Very light loads slowly applied by hand will strip off such films, leaving a thin layer of varnish on the metal. In such cases not adhesion but cohesion of the partially dried varnish is measured and testing at these speeds no doubt gives abnormally high results. The same type of variation was noted by Douglas and Pettifor (*3*) in their study of glue bond strength where their energy-absorption method was used after exposure of specimens to atmospheres of different humidities. This condition offers no difficulty, however, with the thoroughly dried films here discussed, with which the separation is clean and speed of test does not influence the results, at least within any accuracy of importance in varnish testing.

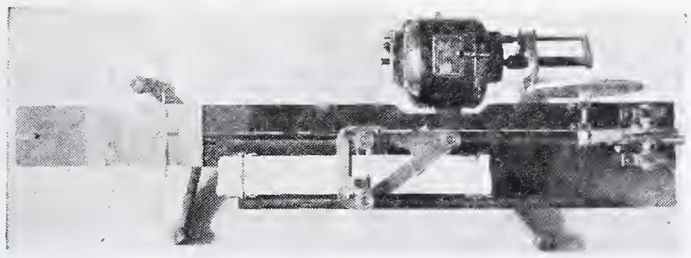

Figure 4. Apparatus Showing Test in Progress

Another question of vital interest refers to the relation between adhesion to aluminum and to other metals. Study is in progress with foils of tin, lead, copper, and zinc. Iron and steel are of course of first importance, but means have not yet been found for studying them.

Conclusions

The method described meets the requirements of a satisfactory test method as follows:

It is reproducible and adaptable to any type of film.

Films may be dried or baked under any conditions before test.

The film is unchanged by treatment before test.

The test does not deform or alter the film.

Results are independent of rate of application of stress.

The test, being graphic, will show inequalities of adhesion over the length of the sample. As the width of the strips is decreased and their number on a single panel is increased, we can to that extent localize areas of varying adhesion.

The test is independent of hardness, brittleness, flexibility, etc.

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Stability of Aqueous Solutions of Boric Acid Used in the Kjeldahl Method

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In a recent paper ["Titration of Ammonia in Presence of Boric Acid," Meeker and Wagner, Ind. Eng. Chem., Anal. Ed., **5**, 396 (1933)] it was mentioned that boric acid solutions suffered deterioration on standing, finally failing to yield a pink color with methyl red. This behavior has now been investigated and is apparently attributable to lack of purity of the distilled water used, revealed by the fact that one lot of freshly prepared boric acid solution was practically neutral to methyl red, the water itself being alkaline. This does not account for the progressive deterioration of other solutions, which could not be studied because none of the water giving such a result was available for examination at the time its probable responsibility was discovered.

A freshly prepared 4 per cent solution of c. p. boric acid in redistilled water was transferred to two bottles, one of lime glass and the other of Pyrex glass, both previously cleaned by steaming out. The fresh solution gave a normal pink color with methyl red under the conditions specified for the ammonia titration. The bottles were kept at room temperature and protected from dust and light. Portions of the solutions were removed at intervals and tested under the conditions of the microtitration: 5 cc. of boric acid solution were diluted with 25 cc. of redistilled water, boiled to remove carbon dioxide, and cooled, 2 drops of 0.05 per cent methyl red indicator were added, and the color was compared with that of a color standard similarly prepared from a freshly made solution of boric acid (using the same lots of boric acid and redistilled water).

The solution kept in Pyrex glass gave after 197 days a color not distinguishable from that of the freshly prepared color standard. The solution kept in lime glass showed no deterioration for 91 days; after 70 days more, the weakening of the color with methyl red was just visible; after a final interval of 36 days the deterioration was measurable, addition of 0.02 cc. of 0.01 *N* acid to the test portion being required to equal the color intensity of the standard. At the end of the test period the pH of each solution was determined using a potentiometric titration outfit with calomel half-cell. The two stored solutions and a fresh solution all showed the same pH. A colorimetric determination of the pH of a fresh 4 per cent solution gave the value 4.1.

This demonstration of the stability of boric acid solution, especially if stored in Pyrex glass, removes a possible objection to the boric acid modification of the Kjeldahl method using methyl red indicator. However, the method described for restoration of solutions deteriorated as first reported has been used repeatedly and is satisfactory. The necessity for such treatment will probably not arise if boric acid solutions are made with distilled water of the quality ordinarily available in analytical laboratories.

Received June 28, 1934.

Determination of Artificial Color in Whisky

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IN THE examination of whisky for color before the prohibition era, the principal test applied for caramel was straight amyl alcohol, which is not now considered a very satisfactory reagent in the light of present knowledge of color tests and reagents. The test was applied by putting about 10 cc. of whisky in a 6-inch (15-cm.) test tube, adding two or three times as much amyl alcohol, and shaking.

Amyl alcohol indicated practically all artificial color that was known at that time, giving a heavy test in the lower layer for coal-tar dyes and caramel, but showed a slightly positive reaction with aged whiskies when no artificial color was present. With the advent of the Marsh test or Marsh's reagent (amyl alcohol plus 3 per cent of phosphoric acid and 3 per cent of water) this reagent improved. It indicated caramel readily and gave a negative reaction for naturally aged whisky, although in some instances giving a very slight test with highly colored, naturally aged, very old whiskies, which experience has taught the analyst to consider as negative. Practically all coal-tar colors that produce a satisfactory brown color with whiskies are indicated positively by the amyl alcohol test, but usually show almost no color in the lower layer with the Marsh test. All coal-tar colored whiskies that have been analyzed in this laboratory gave a negative Marsh test, except that in some instances the lower layer was pinkish in color.

Various coal-tar dyes were mixed in the laboratory in order to produce a satisfactory whisky brown—for example, tartrazine and Bismarck brown. This combination imparted a yellowish brown color to proof alcohol which was Marsh-positive. When whisky is colored with coal-tar dye and the Marsh test is negative, amyl alcohol gives a positive test. When whisky is colored by quick-aging with either charred or uncharred chips, straight amyl alcohol gives a very strong positive test. The usual A. O. A. C. coal-tar double-dyeing tests (*2*) can be used to confirm coal tar, or its presence can be confirmed by drawing off the lower aqueous layer of the amyl alcohol test with the aid of a small separatory funnel into a white porcelain dish and treating with a few drops of strong hydrochloric acid. Usually this causes it to change to red or pink, which can be decolorized completely by a few drops of stannous chloride. Caramel or wood colors show no visible change with these last two reagents.

Zinc Acetate Test for Caramel

Through the use of numerous quick-aging processes, new colors have been developed, one of the most interesting being the reddish brown color extracted from uncharred white oak chips found in some well-known whiskies. This gives a positive reaction with Marsh's reagent, amyl alcohol, Williams' test (*4*) and other tests, including those outlined by the A. O. A. C. It became necessary for this laboratory to find some means of distinguishing this color from caramel. This most satisfactory test worked out in this laboratory, characterized as the zinc acetate test, is applied as follows:

Mark a 150-cc. beaker at 13-cc. and 25-cc. volume. Place in the beaker 25 cc. of spirits to be tested. Add 0.5 cc. of glacial acetic acid and mix, then add 0.75 gram of U. S. P. zinc acetate crystals. Mix, then heat rapidly over a strong flame to vigorous boiling until the volume is reduced to the 13-cc. mark, stirring to prevent spattering. Should the volume be reduced below 13 cc., make up to 13 cc. with water. Set aside to cool gradually. When cool, make up to the 25-cc. mark with 95 per cent alcohol, mix, and let stand several minutes. Then mix and pour through double 15-cm. folded filter paper into cylinder. Mix the filtrate, put 6 cc. into a 6-inch (15-cm.) test tube, and add 12 cc. of Marsh's reagent. Heavy precipitation takes place, but the precipitate will go back into solution if thoroughly mixed. Allow to separate thoroughly, pour off 4 cc. of the upper solution, and replace with 4 cc. of ethyl acetate, 88 per cent grade. Mix thoroughly and allow layers to separate.

The colored lower layer shows caramel or certain coal-tar dye material. If none is present, the lower layer is clear and colorless. Instructions must be followed as directed for the zinc acetate test, as oaks differ and this is the only combination of reagents which works under all conditions. If the test shows a strong positive indication (a reddish shade) and the original liquor gave a negative reaction with Marsh's reagent but was rather pinkish in the lower layer (and the straight amyl alcohol test gave a very heavy positive indication), coal-tar dye is likely to be present. This coal-tar color can be confirmed by adding a few drops of concentrated hydrochloric acid to some of the unused filtrate from the zinc acetate treatment in a small white porcelain dish. This will cause a deep pink color in the presence of certain coal-tar dyes, but by the further addition of stannous chloride the colors produced by the dyes are decolorized. In rare instances the pink color does not appear. In examining these reactions the best results are secured by using as a background the clear light of an open window.

Ferric Alum–Sodium Acetate Test

Another test for whisky that is suspected of being colored with uncharred chips or similar coloring matter is as follows:

To about 10 cc. of the whisky add 2 cc. of a ferric ammonium sulfate solution (1 per cent in water), followed by 5 grams of powdered sodium acetate. Mix, allow to stand for 10 minutes, and filter.

If the color is due to uncharred white oak chips, the solution becomes an intense blue-black on the addition of the ferric ammonium sulfate, but the filtrate is without color. Sometimes the filtrate is slightly bluish, becoming colorless on being warmed gently and poured through the filter several times.

If caramel is present, warming and refiltering does not affect the color. After the addition of ferric ammonium sulfate there is no color change or any pronounced change when 5 grams of sodium acetate are added, but the brown color of caramel comes through the filter paper in the usual manner. If the whisky was colored by quick-aging with charred or toasted oak chips, the filtrate is colored as in the case of caramel. If the color is due to natural aging in wood over a period of years, such as a sample of Bottled in Bond, the filtrate is colored.

Whiskies that are colored with uncharred white oak chips give a positive reaction with the A. O. A. C. paraldehyde test for caramel (*1*); they also give with the A. O. A. C. caramel test (*3*) a more positive reaction than when caramel is actually used to produce the same depth of color. This new form of color, which is easily extracted from white oak chips with hot or cold proof alcohol, is different from color produced by slow-aging in charred barrels or by ordinary quick-aging in the presence of toasted or charred chips. This extract has a reddish cast and with Marsh's reagent shows all the color in the lower aqueous layer. In order to prove that this color was not due to caramel, the following test was devised:

To 5 cc. of liquor add approximately 1 gram of calcium chloride and shake continuously until it has dissolved. Allow to cool, and then add Marsh's reagent in the same manner as in making the Marsh test. After shaking, allow to stand. The color which had been found in the lower aqueous layer lifts and forms a brown zone between the amyl alcohol and aqueous layer, leaving the bottom aqueous layer usually quite colorless.

A sample of uncharred white oak chips was found, the color of which it was difficult to remove with calcium chloride. For this reason this method has been abandoned in favor of the zinc acetate method outlined above, which has been proved the most satisfactory test for this purpose yet known. The calcium chloride test is retained for its value in indicating the quick-aging treatment. A heavy brown ring that settles between the amyl alcohol layer and the aqueous layer is formed with whiskies that have been treated with either charred or uncharred chips.

In testing for source of color in whisky, the following order is suggested:

1. Marsh test.
2. Amyl alcohol test.
3. If the Marsh test is positive, the zinc acetate test should also be applied; the lower layer will be colored if caramel or certain coal-tar dyes are present. Apply the simple coal-tar confirmatory test; if the color cannot be decolorized it is due to the caramel. If the lower layer is negative (colorless), the original color is due to uncharred or imperfectly charred wood.

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Melting Point Apparatus with Rapid Mechanical Stirring

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During the past several years the author has had occasion to make numerous determinations of the melting points of various organic compounds, especially higher paraffin hydrocarbons. In the course of these investigations certain discrepancies were noted in the values of the melting points taken with different types of melting point apparatus. For example, it was found during a thermal study of 3-phenyl-2,4-thiazolidione by means of heating and cooling curves that one form of the compound melted at 147° to 148° C., as determined by the capillary tube method employing an electrically heated air bath (*3*), whereas in the thermal apparatus (stirred oil bath, *1*) the product melted at 146° C. as measured with a thermocouple and 146° to 147° C. as measured with a thermometer. A similar discrepancy was noted in the melting points of *n*-nonacosane (*2*) determined in an electrically heated air bath (65.1° C.) and in an oil bath stirred at high speed (63.5° to 63.7° C.).

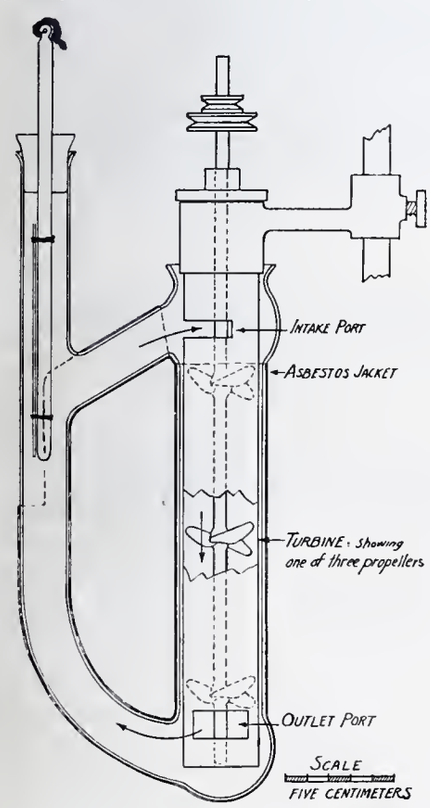

Figure 1. Modified Thiele Tube and Turbine Pump Assembly

These and other similar observations indicated that the melting points were influenced by the rate and mode of heat transfer within the apparatus. The melting points of a series of organic compounds were determined in a number of well recognized forms of melting point apparatus which differed principally in the manner of heat interchange. It was found, other conditions being the same, that unstirred air baths gave the highest, and high-speed mechanically stirred oil baths the lowest, values for the observed melting points, whereas intermediate stirring rates (hand-operated devices) gave intermediate values. All apparatus depending on air for the thermal conduction medium gave higher values than those employing a liquid medium.

During these studies a number of modifications of standard apparatus were devised with the view of attaining satisfactory high-speed stirring of the thermal conduction medium. The apparatus shown diagrammatically in Figure 1 was found to meet the requirements of accuracy, simplicity in construction, and ease of manipulation. The principle involved is that of the Thiele tube modified to permit high-speed stirring.

The Thiele tube of Pyrex glass consists of two arms of dissimilar size, both open at the top. The larger arm contains the pump and the smaller one the thermometer and sample. The pump is in reality a commercially available high-speed turbine stirrer, completely enclosed except for the inlet and outlet ports near the top and bottom. The larger arm of the Thiele tube is expanded to form a bulb at the bottom and an annulus at the top at the height of the upper inlet port of the pump. A thin film of oil separates the casing of the pump from the inside wall of the Thiele tube, thus insuring positive circulation through the arm containing the thermometer, immersed to bring the mercury bulb slightly below the bottom of the opening of the cross arm. With the use of a high-grade heavy petroleum oil, determinations of melting points up to 225° C. can be made. Melting point–bath wax may be used to attain temperatures up to 350° C., provided the Thiele tube is wound with sufficient asbestos-covered resistance wire to permit preliminary melting of the wax.

The apparatus holds approximately 250 ml. of oil which may be circulated at a maximum velocity of 5 liters per minute. Ordinarily, however, a pump speed of 1500 r. p. m. is sufficient to insure adequate circulation of the thermal conduction medium.

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Volumetric Determination of Tungsten

A Study of the Method Proposed by Dotreppe

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ALTHOUGH it has been quite generally accepted that a satisfactory volumetric determination of tungsten based on a reduction and subsequent oxidation is impracticable (*2*), the method proposed by Dotreppe (*1*) appears simple and very accurate. The present author, having need for a rapid determination of tungsten, thought it worth while to repeat the work and investigate its possibilities.

The method of Dotreppe involves reduction of an alkali tungstate by zinc and concentrated hydrochloric acid in an atmosphere of carbon dioxide, oxidation with ferric alum, titration of the resulting ferrous iron by permanganate, and calculation based on an apparent reduction of WO_3 to W_4O_7. The results reported show that 99.6 per cent of the tungsten, the average of the nine values included, was recovered.

Table I presents results obtained when the method cited above was followed as exactly as possible.

Table I. Results Using the Dotreppe Method

Sample	Number of Trials	Variation in Tungsten Recovered	Average Recovery
		%	%
K_2WO_4 + KCl	17	65 to 94	85
K_2WO_4	6	74 to 94	84
Na_2WO_4	16	79 to 98	93

Modified Procedure

These poor results were apparently due to difficulties in the reduction of the tungstate and to a lack of sharpness in the permanganate end point. The end point was obscured by a flocculent precipitate of pale yellow hydrated tungstic acid which appeared when the solution was diluted before being titrated. Conditions of reduction were kept as exactly alike as possible, although variations in time, temperature, concentration of the acid, and amount of zinc were tried. A sharp end point was obtained by reduction of the tungstate in the presence of a small amount of phosphoric acid and titration of the ferrous iron with potassium dichromate, using diphenylamine sulfonic acid indicator prepared and used as suggested by Sarver and Kolthoff (*3*). Phosphoric acid prevents the precipitation of tungstic acid, but still has no influence on the reduction or on the reduced compound (*1*). Table II presents results obtained by using this modified method.

Table II. Results Using the Dichromate Method

Sample	Number of Trials	Variation in Tungsten Recovered	Average Recovery
		%	%
K_2WO_4 + KCl	12	71 to 97	86
K_2WO_4	6	88 to 98	93
Na_2WO_4	12	75 to 90	80

These again were very poor, even though the end point was quite clearly defined.

Conclusion

This proposed volumetric determination of tungsten has been found unsatisfactory mainly because of the apparent impossibility of obtaining consistently identical reductions of WO_3.

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A Simple Laboratory Apparatus for Vacuum Distillation

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ALL the current types of receivers for collecting the successive fractions of a condensate from a vacuum distillation without interrupting the operation apparently trace their origins to one of two precursors: One is the Thorne "triangle" (*5*), the other is either the Gorboff-Kessler vacuum desiccator (*4*) with revolving table, or its modification, the Brühl apparatus (*2*), which appears to have been accepted to the exclusion of its predecessor. It in turn seems to have inspired the less cumbersome, compact Bredt "star" device (*1*) or its antecedent, a receiver described by Gautier (*3*). The triangle types are not well suited for sharp separations where quantitative analyses are involved. For this purpose the Brühl and star receivers are superior.

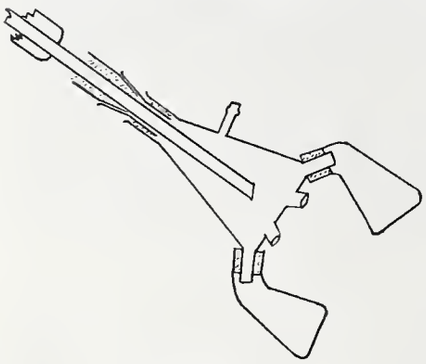

Figure 1

The need, arising during the course of the fractionation of methyl esters of fatty acids in the analysis of oils, for a small receiver with tubes not too large to be weighed on an analytical balance, yet readily stoppered for storage, led to the construction of a device (Figure 1), patterned after the von Wechmar (*6*) apparatus, from one 250-cc. and six 50-cc. Erlenmeyer flasks and a ground-glass joint. Because of its simplicity of construction and efficiency of operation—a 3-mm. vacuum can easily be maintained in the system and a recovery loss of less than 0.3 per cent is not unusual (Table I)—it is described here, in the hope that others may find it a useful tool in the analysis of fatty oils or in other fields.

An outlet tube, through which the system is evacuated, is sealed into the side of the Erlenmeyer flask. Equally spaced around the periphery of its base are sealed six 10 × 40 mm. outlets to which the receivers are subsequently attached by means of rubber stoppers. One is not necessarily limited to six openings, and ground-glass joints may be substituted for rubber stoppers. The receivers are made by giving the neck of a 50-cc. Erlenmeyer flask a 90° bend. Into the neck of the large flask a

female 0.75-inch (1.9-cm.) ground-glass joint, is fitted by means of a rubber sleeve, or, if preferred, joint and flask may be sealed together. The male joint is similarly treated with respect to the condenser, but in any case the system is so assembled that the end of the delivery tube is brought directly over one of the individual receivers so that the droplets of distillate fall directly into the receiver without wetting the sides of the neck.

Table I. Fractional Distillation of Methyl Esters of Fatty Acids[a]

Fraction	Boiling Point at 3 mm.	Weight
	° C.	Grams
1	155–165	2.8352
2	165–169	2.9516
3	169–172	3.1822
4	172–183	3.1590
	183+	1.4704
	Taken	13.6370
	Recovered	13.5984
	Loss	0.0386
	Percentage loss	0.30

Courtesy of Thelma Garvin.

This apparatus has given most satisfactory service in a 3-year trial in the hands of advanced students. It is rugged, requires the services of no expert in its construction, is not costly to make, and takes up little space on the desk. Its dimensions and number of receivers can be varied to suit the needs of the operator.

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Ceric Sulfate for Estimating Tin in Bearing Metals

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In the usual method for estimating tin in bearing metals, the stannous tin is oxidized in hydrochloric solution with standard iodine solution which must be standardized against pure tin and checked frequently. H. H. Willard, N. H. Furman, and others in a series of papers in the *Journal of the American Chemical Society* from 1928 to 1934 have pointed out the advantages of ceric sulfate as a standard oxidizing agent. It may be used in hydrochloric acid solution and retains its original concentration over a long period of time. In the present investigation the procedure as described by Hallett (*2*) was followed except that 0.1 *N* ceric sulfate was used as the oxidizing agent, using as indicator 5 ml. of a solution made by dissolving 1 gram of soluble starch and 10 grams of potassium iodide in 100 ml. of distilled water. It was also found that better results were obtained if 0.1 gram of antimony was dissolved with the sample.

Runs were made on pure mossy tin with the results shown in Table I.

Table I. Estimation of Tin

Tin Sample	Tin Found	Tin Sample	Tin Found
Gram	*Gram*	*Gram*	*Gram*
0.1032	0.1027	0.1082	0.1080
0.1003	0.1001	0.1362	0.1363
0.1080	0.1084	0.0996	0.1003

In order to test the validity of the method on actual bearing metals containing possible interfering elements such as copper and arsenic, runs were made on Bureau of Standards bearing metal samples, Nos. 53 and 54. No. 53 is a lead-base bearing metal containing 10.94 per cent of tin, and No. 54 is a tin-base bearing metal containing 88.24 per cent of tin. The results obtained are given in Table II.

Table II. Estimation of Tin in Bearing Metals

Sample No. 53		Sample No. 54	
Weight of sample	Tin found	Weight of sample	Tin found
Gram	%	*Gram*	%
1.0027	10.89	0.1904	88.23
1.0010	10.87	0.1017	88.58
1.0018	10.94	0.1927	88.06

From these results it appears that ceric sulfate may be used as the standard oxidizing agent in the analysis of tin in bearing metals with results precise to from one to four parts per thousand.

The theoretical titer obtained by standardizing against anhydrous sodium oxalate (*1*) may be used. The solution does not have to be restandardized over a long period of time. In the authors' work, extending over a period of 3 months, the solution did not change appreciably.

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Cyclohexanol in Colorimetric Determination of Molybdenum

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During the course of a study of the variables involved in the colorimetric determination of rhenium it was found that the presence of small amounts of ether exerted an appreciable influence upon the development of the color. Ether is generally used to extract the thiocyanate-rhenium complex and it was thought that perhaps the erratic results often obtained might be due to an interaction of the ether and the rhenium thiocyanate or to an alteration accelerated by the ether. Accordingly a search was made for more inert extraction media. It was found that cyclohexanol exerted practically no influence upon the reaction and that the colored complex was unusually soluble and stable in this solvent.

Inasmuch as the conventional colorimetric method for molybdenum is identical with that for rhenium, it seemed probable that the same factors which contributed to the unreliability of the rhenium determination might account for some of the peculiarities often encountered with molybdenum. Cyclohexanol, like butyl acetate, is a better solvent for the thiocyanate than ether or ether mixtures. Consequently

smaller volumes of these menstrua are required for extraction and both have the decided advantage of lower volatility. Cyclohexanol exhibits little tendency to decompose at room temperature and, unlike butyl acetate, its hydrolysis products do not promote color fading. It may be recovered from residues by neutralizing the free acid and distilling under reduced pressure.

Solutions of stannous chloride and potassium thiocyanate were prepared in the manner described by James (*1*). The cyclohexanol was of the commercial grade marketed by E. I. du Pont de Nemours & Co., Inc., and was used without further purification. Prior to use it was allowed to stand in contact with a solution containing stannous chloride, potassium thiocyanate, and hydrochloric acid. The ether was treated as described by Maag and McCollum (*3*). Analyses were made according to James (*1*), the exception being the substitution of cyclohexanol as an extractor. For purposes of comparison, samples of each material were analyzed by the ether extraction method (*2*). Table I gives a series of results obtained on a number of Bureau of Standards steels and molybdenum-containing materials. Standards for comparison were in all cases steels or materials of approximately the same composition and molybdenum content. In some cases where proper standards were unobtainable, known amounts of molybdenum were added to solutions of the same type as those being analyzed. Analysis of solutions of ammonium molybdate and of synthetic mixtures yielded excellent results.

Table I. Determination of Molybdenum

Sample, U. S. Bureau of Standards	No. of Determinations	Molybdenum Present	Molybdenum Found	Av. Deviation	Error	Extractor
		%	%	%	%	
Cr-W-V No. 50	5	0.01	0.010	0.0002	0	Cyclohexanol
	3	0.01	0.009	0.0008	10	Ether
Cr-Mo-Al No. 106	4	0.164	0.163	0.002	0.6	Cyclohexanol
	2	0.164	0.162	0.002	1.2	Ether
Stainless No. 73	3	0.005	0.005	0.0000	0.0	Cyclohexanol
	3	0.005	0.005	0.0001	0.0	Ether
Ferrotungsten No. 75	3	0.23	0.23	0.001	0	Cyclohexanol
	2	0.23	0.24	0.007	4.3	Ether
Ferrovanadium No. 61	3	0.72	0.68	0.002	5.5	Cyclohexanol
	2	0.72	0.67	0.021	6.9	Ether
Spiegeleisen No. 66	3	0.005	0.005	0.0001	0.0	Cyclohexanol
	3	0.005	0.005	0.0001	0.0	Ether
Manganese metal No. 67	3	0.015	0.015	0.0001	0.0	Cyclohexanol
	3	0.015	0.014	0.0002	6.6	Ether
Ferromanganese No. 68	2	0.009	0.009	0.0001	0.0	Cyclohexanol
	2	0.009	0.010	0.0003	9.9	Ether
Chrom-molybdenum No. 72	2	0.149	0.151	0.001	1.3	Cyclohexanol
	2	0.149	0.152	0.001	2.0	Ether

Acknowledgment

The authors are indebted to Arthur R. Stephens who assisted in checking the method.

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Precipitation of Barium in the Copper-Tin Group of Qualitative Analysis

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Prior to 1920 it was the usual practice in qualitative analysis to precipitate the copper-tin group by introducing hydrogen sulfide into a hot solution containing a little free hydrochloric acid. Students were warned not to pass hydrogen sulfide into a solution containing nitric acid or aqua regia.

In the 1920 edition of Noyes' excellent text (*1*), nitric, rather than hydrochloric, acid is recommended for dissolving solid substances, making the solution 0.3 *N* in nitric acid before precipitating with hydrogen sulfide. Except when arsenic is present, the precipitation takes place in the cold.

Arsenic forms very insoluble sulfides. Although arsenic sulfide cannot be dissolved appreciably by hot hydrochloric acid, it is precipitated very slowly from cold, dilute acid solutions of an arsenate. Noyes recommends, therefore, filtering off the precipitates that form on passing hydrogen sulfide into the cold solution, heating the filtrate to about 90° C., and introducing more hydrogen sulfide. If a yellow precipitate forms slowly from the hot solution, strong hydrochloric acid is added, the solution is evaporated to dryness and, after adding more hydrochloric acid, is saturated with hydrogen sulfide first in the cold and later at 70° to 90° C. This procedure has been copied into other textbooks (*2*).

In working with solutions containing 40 mg. of arsenic as potassium arsenate and 40 mg. of barium as chloride, several students in qualitative analysis recently failed to find any barium. After testing all the precipitates obtained in the analysis, it was eventually found that the barium had been precipitated as barium sulfate during the precipitation with hydrogen sulfide.

If a solution containing arsenate in 0.3 *N* hydrochloric acid is treated with hydrogen sulfide at 90° C., a precipitate of arsenic sulfide soon forms and no appreciable dissolving of the precipitate takes place when the solution is evaporated to dryness after adding some concentrated hydrochloric acid. If the experiment is repeated with a solution which is 0.3 *N* in nitric acid at the start, the precipitate of arsenic sulfide sometimes disappears completely during the evaporation. If the solution contains barium ions, these are precipitated as barium sulfate, while the arsenic sulfide is dissolving.

A series of experiments was carried out with varying quantities of arsenic and of barium, following as closely as possible the procedure recommended by Noyes for precipitating the copper-tin group. In the absence of a precipitate of arsenic sulfide there was no precipitation of barium. During the evaporation with hydrochloric acid, the excess hydrogen sulfide is boiled off before the nitric acid or aqua regia becomes strong enough to oxidize sulfide to sulfate. When this oxidizing acid becomes concentrated sufficiently to dissolve arsenic sulfide, it is also strong enough to oxidize sulfide to sulfate.

The danger of forming barium sulfate during precipitation with hydrogen sulfide can be avoided by using hydrochloric instead of nitric acid to make the solution 0.3 *N* in mineral acid before treating with hydrogen sulfide or by filtering off any arsenic sulfide precipitate before removing nitric acid by evaporation with hydrochloric acid.

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Received September 1, 1934.

Sintered Pyrex Glass Aëration Tubes

R. D. Cool[1] and J. D. Graham, Laboratory of Pharmacology, University of Pennsylvania, Philadelphia, Pa.

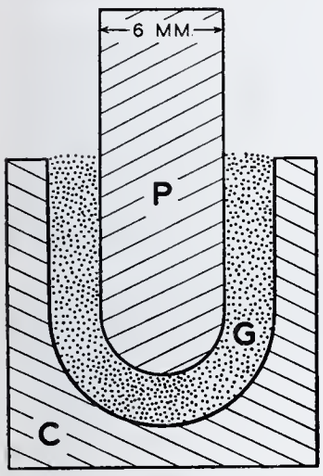

Figure 1. Section through Mold for Sintering Powdered Glass

C, Cup bored from 15-mm. graphite rod; *G*, powdered Pyrex glass; *P*, plug made from 6-mm. arc lamp carbon.

The applications of sintered Jena glass disks have become well known through their wide use in filtration and in gas absorption apparatus (*3*). Recognition of the desirability of constructing similar devices from Pyrex brand glass has resulted in several articles (*1*, *2*) dealing with this subject. In some cases shapes other than the well-known disk seem desirable. For dispersing gases into fine bubbles in liquids, for ready saturation of the liquids, or for rapid and quantitative absorption of constituents of the gases, the thimble-shaped alundum gas absorption spreaders have proved very effective when applicable. In the course of work in this laboratory it became desirable to devise an apparatus for the quantitative absorption in strong alkali of a vapor mixed with steam, and the authors succeeded in preparing a highly satisfactory gas disperser from Pyrex brand glass which, under such conditions, seemed to offer marked advantages over one made from alundum.

Pyrex glass tubing was crushed in a porcelain mortar and separated into portions by screening. Powdered glass of the desired size (80 to 100 mesh was used in the particular case mentioned) was placed in a mold of graphite (Figure 1) and packed by tapping the mold. The mold and glass were placed in an electric muffle furnace maintained at white heat (1200° to 1400° C.) for 30 to 40 seconds, until a distinct red color had crept completely over the outside of the mold cup, *C*. The mold was then removed from the furnace and the inner carbon plug, *P*, withdrawn. By this initial heating the glass had sintered just enough so that the plug could be removed without destroying the form of the glass thimble. If the sintering was completed without removing the inner plug, so much shrinking of the glass took place that it was practically impossible to remove it. As soon as plug *P* had been removed, the outer cup, *C*, of the mold and the powdered glass, *G*, were replaced in the furnace until the color of the mold just approached that of the oven. This usually required an additional 30 seconds. The mold and sintered glass thimble were then removed from the furnace. On cooling, enough shrinkage of the glass had occurred so that it readily dropped from the inverted mold.

Because the mold, glass, and oven undergo unequal cooling effects during various parts of the procedure, more uniform results could be obtained by using the appearance of the mold and of the glass rather than a definite period of heating as the criterion for completion of the sintering. The whole sintering process, including packing of the mold and removal of the finished thimble, requires about 5 minutes, and by using several molds, so that no waiting is required for cooling, a number of thimbles can be made in a reasonably short time.

If the thimble is wrapped to within 3 mm. of the open end with asbestos paper tape, it can be sealed to Pyrex glass tubing in the usual manner.

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Received July 20, 1934.

Gas-Absorption Bulb for Use with Small Amounts of Reagent

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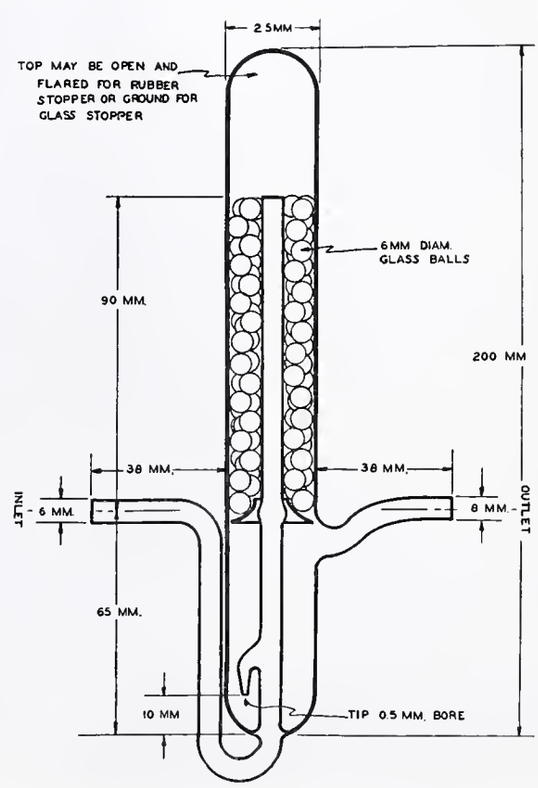
Recently the writer had occasion to make a quantitative study of the oxidation of minute amounts of nitric oxide in coke-oven gas and gum formation resulting therefrom. The investigation included a critical examination of the analytical method described by Schuftan.[1] Testing such a method naturally involved making synthetic samples by adding small amounts of nitric oxide (< 1 p. p. m.) to coke-oven gas free from nitric oxide.

As in all ultrasensitive work, it was desirable to use as little reagent as possible. It was also necessary to keep back-pressure in the system to a minimum, and to accomplish this under conditions requiring unusually thorough scrubbing combined with considerable capacity. Since no absorber on the market would fulfil all these demands, a special bulb (shown in the illustration) was designed. (The glass-blowing required in developing this absorber was done by F. Pierce-Noble, 110 Benham Ave., New Haven, Conn.)



[1] Schuftan, Paul, *Brennstoff-Chem.*, **13**, 104–8 (1932).

The scrubbing is done by the bead column wetted with the scrubbing solution which is pumped over the beads in closed cycle. By the arrangement of the tubing in the apparatus the gas sample is caused to do the pumping. The gas enters through a 6-mm. tube bent in the form of a trap, in which there is a carefully made orifice (0.5 mm. in diameter) situated below the liquid level. Through this orifice the scrubbing solution seeps into the trap, is quickly driven to the top where it is sprayed upon the bead column, and slowly finds its way down to the reservoir whence it came. The bulb may be sealed at the top or closed by a stopper of glass, rubber, etc. For gravimetric work, glass wool may be used instead of beads.

The bulb can most readily be washed with a solution from a gravity reservoir fitted with a rubber tube and pinchclamp. After the solution has been let in, and before disconnecting, the tube is pinched between the bulb and the clamp to collapse it. This will prevent an annoying drip from the tube upon disconnecting. The bulb could doubtless be used for extremely low rates of gas flow by reducing the internal diameter of the 6-mm. inlet tube.

For any given assembly, the height of the scrubbing solution above the orifice modifies within narrow limits the rate of pumping the solution. In most cases the rate should be such as to spray the solution over the beads, since flowing results in flooding which in turn causes loss of effective surface and efficiency.

Gas passed through this bulb at a rate of 1.0 to 1.5 cubic feet per hour (approximately 30 to 45 liters per hour) develops a back-pressure equivalent to less than 0.5 inch (13 mm.) of water. It can be designed to use less than 5 ml. of scrubbing solution. The scrubbing efficiency and capacity have proved to be entirely satisfactory.

In two tests made upon the absorption efficiency of these bulbs, the rate of gas flow was between 1 and 2 cubic feet per hour. In one case a bulb charged with 20 per cent sulfuric acid was subjected to a gas flow carrying a fairly high concentration of ammonia (similar to raw coke-oven gas). On the outlet of the bulb a trap was placed containing 0.1 ml. of 0.1 *N* sulfuric acid, in a little water colored with methyl orange. After 0.5 hour when the test was stopped, the solution in the trap had not changed color. Upon titrating the solution in the bulb it was found that the acid had become so nearly spent that only 0.2 ml. of 1 *N* sodium hydroxide was required to neutralize it.

The second test was a series of determinations of nitrogen tetroxide in gas. Nitric oxide was added in fractional parts per million to the gas which was then treated as in the Schuftan procedure. Two bulbs charged with *m*-phenylene diamine solution were placed in the outlet in series arrangement. More than 95 per cent of the nitric oxide was accounted for in the first scrubber.

Received August 18, 1934.

A Salt Bridge for Use in Electrometric Measurements

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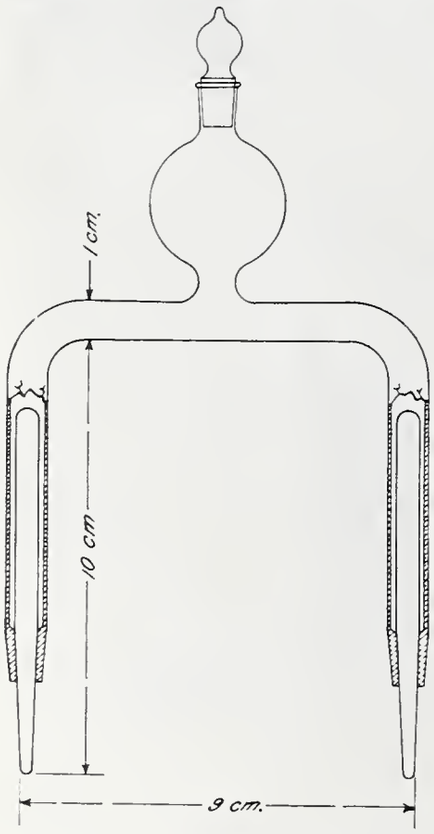
In making a large number of routine pH determinations on soils and other materials by means of the quinhydrone electrode, the faults of the commonly used agar bridge became so troublesome that the authors searched for a more suitable bridge. The bridge finally adopted has proved very satisfactory for their work and is offered with the hope that it may prove useful to others who employ electrometric methods.



The bridge shown in the figure is a modification of that described by LaMer and Baker (*4*, *5*), and is based upon ideas presented by Crowther (*1*), Cupr (*2*), Köhn (*3*), and Schollenberger (*6*). It is made of heavy-walled Pyrex glass tubing of about 1 cm. diameter. The plugs are of Pyrex glass rod and are ground into the tapered ends of the bridge. The bulb is about 4 cm. in diameter and has a capacity of about 25 cc.

For use the bridge is filled to the ground-glass stopper with saturated potassium chloride solution; the plugs are loosened momentarily to insure a film of potassium chloride in the ground-glass joints, and then are seated firmly. The tips are washed thoroughly with distilled water and dried with filter paper to avoid dilution of the reference half-cell. Between determinations the washing and drying of the tips are repeated, but it is not necessary to renew the potassium chloride film in the ground-glass joints.

LaMer and Baker (*4*) have presented proof that the ground-glass form of junction gives a strictly reproducible potential and effectively prevents interdiffusion of saturated potassium chloride and quinone substances. The authors have compared the ground-glass with the agar bridge and have found them to give identical results in buffer solutions, soils, and culture media. The new type of bridge has been used successfully and conveniently in several thousand pH determinations.

Several advantages are apparent in this form of bridge: Preparation of the bridge for the day's work involves only filling with saturated potassium chloride solution; one filling of the bridge is sufficient for an unlimited number of determinations; between samples the bridge is easily and thoroughly cleaned by a stream of distilled water from a wash bottle and easily dried with a small piece of filter paper; and no special arrangements are necessary for keeping the bridge when it is not in use, the potassium chloride being simply removed and the bridge filled with distilled water.

The only caution to be observed in the use of this bridge is to avoid allowing the tips to dry out, else they may stick. If this happens, the joints may be loosened by soaking in warm water and by tapping gently on a solid surface. After loosening, they should always be well seated before proceeding; once seated, they are not easily loosened even if struck accidently against any part of the apparatus. While a determination is being made, the weight of the bridge is supported at the shoulders so that the tips are held several millimeters from the bottom of the vessel. In this position, the contents of the electrode vessel may be stirred without dislodging the plugs.

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